#### NORTHWESTERN UNIVERSITY

### Dielectric Thin-Films by Ion-Beam Sputtering Deposition for III-V based Infrared Optoelectronic Imaging

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### Abstract

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The growing technological industry is demanding the development of powerful and smaller devices. Dielectric thin-films can play an important role to help push towards achieving these goals. However, their advantage of high-quality material and low material costs compared to bulk can only be achieved with consideration of the technique, conditions, and parameters. The sensitivity makes every step in the process extremely important, beginning from substrate preparation to the first initial layers of growth and ending with the testing/modeling of the devices. Further, not all applications want bulk-like properties, so the ability to adjust and fine tune the material characteristics opens up a wide range of opportunities with the advancements and can drive the power of the devices to an ultimate level.

This work provides the motivation, theoretical basis, and experimental results for performance enhancement of optoelectronic devices through the use of high-quality dielectric thin-films by ion-beam sputtering deposition (IBSD). The advantages and disadvantages to this technique are demonstrated and compared to others. The optimization processes, relationships, and motivation of using seven different thin-film materials have been detailed and provided. Using IBSD, the performance improvements were demonstrated on infrared lasers and detectors. For lasers, a 170% increase in maximum output power was achieved using near-0% percent anti-reflection coatings (AR) and near-100% high-reflection (HR) coatings. Following, wide tunability was achieved by using the structures in an external cavity laser system, showing nearly a three-fold improvement in tuning range. Also, structurally robust lasers were achieved with a custom-tailored HR structure designed for damage resistance to high output power density operation, showing over 14W of peak output power for MOCVD lasers. For infrared photodetectors, over a 4 orders of magnitude decrease in current density and zero-bias resistance area product values on the same order of magnitude as bulk are achieved with passivation that was fine tuned in its electrical behavior. In addition, 62% improvement in quantum efficiency for room temperature operation of the detectors was shown with the utilization of a broadband AR coating. Finally, applications of the principles and physics for future work in UV based devices are discussed.

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## CHAPTER 1

## Introduction

High-quality dielectric thin films are useful in numerous applications such as superconductors, microelectronics, mirrors, optical coatings, sensors, optoelectronic devices, semiconductors, X-ray optics, divisional wave multiplexer, surface acoustic wave amplifiers, and broadband filters.



Figure 1.1: Applications that use dielectric thin-film materials

An overview of the work given in this documentation can be described as continuous cycle, as shown in Figure 1.2. The cycle begins with the thin-film growth process and follows with material characterization. Once the thin-film material(s) are appropriately optimized, they are applied to the optoelectronic devices. Following, this leads to device testing used to demonstrate the performance improvements that can be achieved. Simultaneously while the devices are tested, they are modeled using theoretical simulations and compared to experimental results. Any deviations away from theory can result from unexplained behavior and unexpected challenges.

The design and optimization of thin-film materials involves a great amount of work from theory to characterization to experimentation. Further the appropriate material(s), material characteristics, and material quality are dependent on the device and targeted performance goals. Chapter 2 discusses the IBSD system and provides the sputtering physics and modeling needed in order to understand and accurately predict the outcome. This technique has many advantages over others including the ability to achieve highquality films at low-deposition temperature, ability to use almost any material, and the great amount of flexibility from independent operation of the ion sources. While the model for sputtering physics is extremely useful, deviations from the model can occur especially if the conditions of the chamber, target material, and substrate are not ideal. Therefore, Chapter 5 is used to provide experimental information of the relationship between the material properties and the system parameters.

The applications used in this work and at the Center involve a wide array of wavelengths, targeted objectives, and different characteristics. This leads to the need of a mul-



Figure 1.2: Continuous cycle of the thin-film growth process and application to optoelectronic devices for the work discussed.

titude of thin-film materials. The properties and caveats with the materials are provided in Chapter 4. Each material used in this work was chosen for specific reasons such as high dielectric breakdown strength, structural robustness, good thermal stability, appropriate refractive index, or near-vertical etch profile. Each material has its advantages, disadvantages, and, in some situations, a combination of multiple materials is needed. The films must be properly characterized in order to understand and predict their behavior. There are a number of different characterization methods that were used to study the structural, electrical, and optical properties of the dielectric material only, dielectric-semiconductor interface, and their environment-dependent properties. Some of these methods are different from tools typically used in semiconductors, and therefore a separate discussion is given in Chapter 3.

Chapter 7 and Chapter 8 then discuss and provide the pertinent background for two main applications: optical coatings and surface passivation. In addition to background, theoretical simulations, performance improvements, and experimental challenges are also discussed. Following, Chapter 9 provides an outlook and background of future projects with UV based devices.

## **CHAPTER 2**

## Ion Beam Sputtering Deposition

The properties and quality of dielectrics is largely dependent on the type of technique used and the growth conditions. Due to its advantages, an IBSD system was utilized to achieve the performance improvements seen in this work. This chapter provides the information on how to utilize an IBSD system and understand the atomic level physics of the deposition process. Section 2.1 provides an overview of the features and components of the system used in this work. Section 2.2 discusses experimental preparation and procedures. Section 2.3 then goes into detail with the physics of sputtering and the interactions that occur at every step in the sputtering process. The information here can then be used to model the behavior of the ions and atoms during the deposition process to achieve the desired outcome. Finally, Section 2.4 proves the advantages of the IBSD system by comparing its characterization results with other systems.

### 2.1 System Features

IBSD is a physical vapor deposition technique that uses bombardment and collisions to remove a material from a target source. The IBSD system used in this work was an Oxford IonFab 300 Plus, as shown in Figure 2.1. The right side photo shows the inside of the chamber, the bottom of the substrate holder is shown on top, and the circular white object in the middle is the target. The system is equipped with many different features such as controlled substrate temperature from 20 - 400  $^{\circ}$ C and chamber heating up to 80 °C. Multiple materials can be deposited due to a target block that can hold up to 4 target simultaneously, and accurate layer thicknesses can be achieved with the dual crystal monitor system. Further, the configuration of the substrate holder allows up to 6" wafers deposition with excellent uniformity from substrate rotational speeds up 20 rpm. In addition to uniformity, the repeatability is not an issue because of accurate impedance matching with an automatic matching unit (AMU). Enhanced material quality is achieved from a number of different factors such as independent ion source control, utilization of a secondary assistance source, and minimal contamination from the high vacuum chamber and loadlock. The independent control of ion sources allows isolation of the neutralized ion beam energy, direction, and current from the acceleration voltage(1). Finally, one last useful capability of the system is also ion-beam etching.

A schematic drawing of the inside of the chamber is shown in Figure 2.2. The primary deposition source faces the target and the ion-beam hits the material at a 45° angle. The substrate is clamped and rotated upside down facing both the target and the secondary



Figure 2.1: Photographs of the IBSD system used in this work and the inside of the deposition chamber viewed from the primary source

assistance ion source at the same time. Typical substrate-to-source angles range from  $0^{\circ}$  -  $35^{\circ}$  which means that substrate-to-target angles are from  $10^{\circ}$  -  $30^{\circ}$ .

Figure 2.2 also shows the components in the ion sources. Both sources were constructed identically, with the two exceptions: grids and gases. The primary source has grids with small circular apertures that form an elliptical shape with a slight concave curvature to focus the ion beam onto the target. This is different from the assist source grids, which is flat and circularly shape to provide overall coverage of the substrate surface. In addition to the grids, the gases used in the sources can also differ. In this work, Argon was chosen as the sputtering gas. Any inert gas can be chose, but higher sputtering yield can be achieved with Argon because of its large mass difference with other atoms and molecules. Oxygen gas can also be introduced with the Argon sputtering gas, especially useful for cases such as reactive sputtering. More information on reactive sputtering is provided in Section 6.2.1. In the secondary assistance source, argon, oxygen, and nitrogen are used



Figure 2.2: Left side illustration shows the system chamber and the right hand illustration is of the RF ion source. The four major system components of the system include two RF ion sources, one directed at the target and the other directed at the substrate, the substrate, and the target itself. Other components include a high speed maglev turbo pump, gases fed through the sources, and high power neutralizers located outside the sources

where the appropriate selection of which gas to use is dependent on the material. While these three gases were chosen based on the materials discussed in Chapter 4, the system is equipped with the option of using a fourth gas.

### 2.2 Experimental Procedure

The properties of the materials are highly dependent on the condition of the system and target prior to and during the deposition process. This section discusses the importance and procedures necessary for proper conditioning of the chamber, target, and substrate. In addition, the calibration procedure is given in order to effectively utilize the crystal monitor for accurate thicknesses.

#### 2.2.1 Chamber and Target Conditioning

It is important that the chamber and target are in good condition, otherwise deposition results will not be as expected. For the chamber, beginning with the lowest base pressure is optimal. The lowest pressure achievable was around  $8 \times 10^{-8}$  Torr, while minimum of  $5 \times 10^{-6}$  is needed in order to fully sustain the plasma. The pressure can be verified using the ion gauge, and further details on the amount of contamination can be observed with the residual gas analyzer (RGA).

The amount of target contamination also has an effect on the material properties, and should be conditioned and cleaned prior to deposition. The surface of the targets can be contaminated from a number of different sources. One source is from the sputtering process where atoms may land onto a different target on the target block. Another is the formation of native oxide that occurs when the targets are exposed to atmosphere. The rate and thickness of the oxidation layer is largely dependent on the reaction of the target material and the atmospheric conditions. Finally, the last source is from trapping of gases. This can lead to a deeper layer of contamination than the other two sources. The depth of penetration of the gases can vary for different sputtering conditions, and is related to the ion energy E as(1):

$$l = 1.1 \frac{W \times E^{2/3}}{\rho} (Z_i^{1/4} + Z_t^{1/4})^2$$
(2.1)

where W and  $\rho$  are the weight and density values of the target, and  $Z_i$  and  $Z_t$  are the

atomic numbers of the ion and target elements. For compound target materials,  $Z_t$  is found by taking the weighted average of the atomic numbers. Comparing all materials used, PbTe and ZnSe have short penetration lengths, whereas materials like SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> have longer depths and therefore require longer conditioning times.

#### 2.2.2 Substrate Preparation

Proper preparation of the substrate is extremely important. Any contaminants on the surface can significantly alter the film growth modes and affect parameters such as adherence, surface morphology, and packing density. The substrate can be cleaned prior to loading into the chamber with acids, such as HF, as is typically done with other types of growths. Additionally, the substrate can also be cleaned off using the ion beam source with bombardment of the ions to remove the first few layers.

The bombardment process is most efficient at lower energy values provided that it is enough to cause desorption of water vapor and gases. The use of the low energy ions is more favorable because this can avoid or minimize any substrate sputtering or structural modifications. If the energy is too high, this can lead to preferential sputtering, alterations in the micro-roughness of the surface, and/or surface damage. Since the layer of the native oxide is typically very thin, only a short amount of time is typically needed for the cleaning process. A typical cleaning procedure involves 15-20 minutes of argon plasma with a power of 10-30 W(2).

Similarly, a reactive gas like oxygen can be used if desiring to deposit a monolayer instead of removing it. One example situation where this is useful is when using the oxide monolayer as an adhesion layer, as described in Section 8.4.1. The time required to remove a monolayer using argon or the time required to deposit a monolayer of oxygen are given as:

$$t_{rg} \simeq \frac{n_f^{2/3}}{\delta z_{rg}} \times j_c \tag{2.2}$$

where  $n_f$  is the surface density,  $\delta$  is the trapping probability,  $z_{rg}$  is the impingement rate, and  $j_c$  is the condensation coefficient. Experimental tests can be done to determine these values.

#### 2.2.3 Thickness Monitoring

An accurate way for monitoring the thickness in-situ is by using a quartz crystal monitor. The crystal monitor works based on the principle that the mass of the films on top of the quartz changes the oscillation frequency. There are three values that need to be set properly to ensure accuracy: tooling factor, density, and z-ratio. These values are pre-defined and are dependent on the target material and lifetime of the crystal.

The tooling factor is a factor used to set the position of the crystal monitor relative to the sample, and is unique for each deposition system used. Calibration of the tooling factor and density is done by setting initial values, and adjusting the value based on the ratio of the measured thickness to the thickness reported by the controller. The initial tooling factor is multiplied by this ratio and the initial density value is divided by this ratio. As the quartz crystal lifetime starts to decrease, the accuracy of the monitor becomes less effective.

Material	Tooling	Density	Z-Ratio
PbTe	152.6	8.140	0.320
$SiO_2$	130.0	2.640	1.000
$\mathrm{Si}_3\mathrm{N}_4$	130.0	2.640	1.1000
$\mathrm{TiO}_2$	113.2	4.260	0.400
$Y_2O_3$	103.1	5.080	1.000
ZnO	100.0	5.610	0.556
ZnSe	103.5	5.266	0.722

Table 2.1: Experimentally determined crystal monitor values

The z-ratio is a parameter that offsets the frequency change relative to the thickness

$$Z = \sqrt{\frac{d_q \mu_q}{d_f \mu_f}} \tag{2.3}$$

where  $d_q$ ,  $d_f$  are the density values of the quartz and the film and  $\mu_q$ ,  $\mu_f$  are their shear modulus values. Table 2.1 provides the tooling factor, density, and z-ratio of the materials used in this work. It was experimentally determined that the crystals should be replaced when a lifetime of 35 - 50% has been reached.

#### 2.2.4 Sample Holder

The use of numerous devices and samples in the system requires a customized design of different holders. Two holders used often for this work are shown in Figure 2.3. The first holder was used for the AR coatings discussed in Chapter 7, with exposure of the laser facet to the deposition. Three different lasers can be fitted within the holder simultaneously, and a razor blade is used to shadow certain areas of the facet. The second holder, shown on the right, was used for top-side deposition on samples by using clips that held the samples

at the corners. Another commonly-used method was to hold the samples with kapton tape onto a solid aluminum carrier plate. The choice of holder is entirely dependent on the sample being deposited on and only three requirements must be met with its design. First, the holder must fit within a 6" carrier plate. Second, the thickness of the carrier plate and holder combined can not exceed 12 mm. Third, the total weight of the holder and carrier plate must not be too light or otherwise the plate will collide with the substrate wafer clamp.



Figure 2.3: Pictures of custom designed holders for the IBSD system

### 2.3 Sputtering Physics

In order to achieve the desired material properties, it is pertinent to have knowledge of the behavior of the ions and atoms during the deposition process. Since IBSD is a physical deposition technique, the basics involve elastic collisions within the plasma. However, this generalized model only works for certain situations, and modeling of the process is much more complicated. For this reason, a single behavior of the particles cannot be
generalized to occur anywhere within the chamber. Instead, the ongoing processes must be considered at each interaction between the ions, atoms, target, substrate, chamber walls, and ion source. This section discusses each one individually in the order that an ion/atom typically travels through.

### 2.3.1 Plasmas and Sheaths

During the sputtering process, the IBSD consists of two sheaths with a plasma in-between. There are many characteristics of plasmas that are important, consisting of many different types of particles: electrons, positive ions, negative ions, atoms, and molecules. The characteristics for each one is given in Table 2.2

Particle	Mass	Temperature	Mean Speed
	[g]	[K]	$[\mathrm{cm/sec}]$
Neutral Argon	$6.6 \ge 10^{-23}$	293	$4.0 \ge 10^4$
Ions	$6.6 \ge 10^{-23}$	500	$5.2 \ge 10^4$
Electrons	$9.1 \ge 10^{-28}$	23,200	$9.5 \ge 10^{7}$

Table 2.2: Characteristics of particles in a plasma

A sheath is a space charge region where the electrical charge density is nonzero. There are two in the system, one surrounding the substrate and the other surrounds the target. Each sheath has a potential voltage drops across it where the charge is negative for the target sheath and positive for the substrate sheath. The charge of the substrate leads to the attraction of ions pulled towards it causing random impingement. The result is a higher ion current density by an amount equal to(3):

$$j^{en} = j^{ion} - qzj_e \tag{2.4}$$

where z is the charge of the particle, and  $j_{ion}$ ,  $j_e$  are the current densities of an ion and electron equal to:

$$j = exp[\frac{\pm qV_a}{kT^{\pm}}] \tag{2.5}$$

and T is the temperature of the atom. Minimizing this value is essential when attempting to lower any amount of surface damage, as will be discussed in Section 8.4.2.

In addition to charge, another difference between the two sheaths is dimensions, where the target sheath has a larger volume. Surrounding the volume of the target sheath is a pre-sheath and this area is similar to the sheath with the exception of having a weaker electric field. The reason why it is important to consider the target sheath is because this is where a significant amount of ionization occurs. Ions will be accelerated through the sheath to undergo charge exchange collisions with neutral species. The energetic argon ion will take an electron from a neutral argon ion, preventing it from being accelerated by the electric field. On the other hand, the new charged argon atom can be accelerated and acquires more kinetic energy in the process. The overall effect is a change in the kinetic energy and density of bombarding particles.

In-between the sheaths is a plasma. The difficulty in understanding plasmas is due to the different characteristics that the particles have, such as the mass of electrons being significantly smaller than neutrals and ions. The plasma is important in that it is essential for generation of the ion-beam. The sustainment process is as follows. An ion must have a high enough kinetic energy to create a charged particle and no longer rely on any external ionization. This energy can be obtained with a having a higher current density. They will then strike the free electrons to create secondary electrons. The secondary electrons are accelerated into the body of the plasma and will strike neutral gas atoms to create ion-electron pairs.

Once generated, the plasma has a potential which represents the steady state condition where the loss of electrons occurs at the same rate as the loss of ions and the net charge is neutral. If the charge is non-zero, the electrons within the plasma will mobilize to eliminate any charge imbalance and effects from the applied electric field. The plasma potential can be found equal to(3):

$$V_p = \frac{-kT^-}{q} ln[\frac{j_e - j_{ion}}{-qz}]$$
(2.6)

This is a general estimate that does not take into account the charge of the chamber walls, but a more detailed model can be found in Ref. (4).

### 2.3.2 Ion Beam

The ion beam is generated by impact ionization in response to the applied fields. The ionization process involves:

$$e^- + Ar \to Ar^+ + 2e^- \tag{2.7}$$

Confinement of the electrons occurs due to the magnetic field and acceleration is due to the electric field. Once the ionization occurs, the beam is extracted from the source chamber by applying a positive potential to the extraction grid. Once removed from the chamber, the particles are accelerated into the deposition chamber by a negative potential applied to the acceleration grid. From this, the electrons will have a higher gain in energy and instantaneous response due to its small mass size.

Once the ions are extracted from the source, they will travel a certain distance before it experiences a collision. If this distance is shorter than the distance to the target, collisions can occur with other particles in the plasma modifying its properties. The average distance the ion will travel before experiencing a collision is called the mean-free path length. The mean free path length is related to the radii of the particles involved in the collision along with the temperature and pressure. In general, ions will have a higher probability of reaching the target without experiencing a collision if the temperature T is high and the pressure P is low. The mean-free path length is given by:

$$\lambda = \frac{kT}{\sqrt{2}P\sigma} \tag{2.8}$$

where  $\sigma$  is the collision cross-section related to the radii as  $\sigma = \pi (r_1^2 + r_2^2)$ . The radii for the different atoms are given in Table 2.3

Finally, the last point to consider is the shape and area of the beam that hits the target. There are three main parameters that affect this: beam current, beam voltage, and accelerator voltage. The changes are shown in the plot of Figure 2.4. The divergence for all conditions, regardless of beam voltage or accelerator voltage, show a general decrease

Atom	Atomic Radius
	$[\mathrm{pm}^{-1}]$
Argon	71
Lead	154
Nitrogen	56
Oxygen	48
Selenium	103
Tellurium	123
Titanium	176
Yttrium	212
Zinc	142

Table 2.3: Atomic radii of several atoms.

with higher beam currents until a minimum angle is reached and then the angle increases. This minimum point occurs at a lower beam current value for lower beam voltages. Furthermore, the range in angles is greater for higher beam voltages. It can be seen that the accelerator voltage causes a shift in the divergence angle, with changes becoming more significant with higher beam voltages. This information should be considered because the angles will affect the change in momentum and scattering angle of the target atoms.

### 2.3.3 Target Surface

At the target surface, elastic collisions will occur between the ions and target atoms. The result of the elastic collision is a change in the momentum for both the ion and target atom and an exchange in energy, as shown in Figure 2.5.

There are a few different collisions that can occur at the target surface. The first is between an electron and a neutral ion or target atom. With this collision, very little energy is transferred from the electron to the ion because of the large mass difference.



Figure 2.4: Plot of the angle of ion beam divergence dependence on beam current, beam voltage, and accelerator voltage



Figure 2.5: Elastic collision between an incoming ion and a stationary target atom showing the change in momentum. Eqs. 2.9 - 2.11 can be used to calculate the velocity and direction of travel of the atoms after the collision.

However, the momentum change of the electron is large. This will lead to a large number of additional electrons due to multiplication. The second is a collision between an electron and an electron. In this situation, the energy exchange is effective since the masses are equal. Finally, the third collision is between a gas atom or ion and a target atom. The change in momentum is related to the velocity of the incoming ion  $v_{ii}$  as:

$$v_{if} = v_{ii}\sqrt{1 - \gamma(\cos\delta_t)^2} \tag{2.9}$$

$$v_{tf} = \frac{2v_{ii}\cos\delta_t}{1 + m_t/m_i} \tag{2.10}$$

$$\delta_i = \tanh[\frac{\sin 2\delta_r}{m_i/m_t - \cos 2\delta_t}] \tag{2.11}$$

and the amount of energy transfer as:

$$T(\delta_t) = \gamma(\cos \delta_t)^2 \tag{2.12}$$

$$\gamma = \frac{4m_i m_t}{(m_i + m_t)^2} \tag{2.13}$$

These equations show how the mass of the ion and target atoms have a large effect on its change in energy and momentum. For example, heavier target atoms, such as Pb, will have a lower amount of energy transferred and a lower velocity after the collision. Further, the angle of the ion after the collision will be smaller so it may continue to propagate through the target material in a forward direction, instead of recoiling. Table 2.4 can be referenced for information on the amount of energy transfer.

The energy transfer is essential for sputtering because the extra energy can help to give the atom a kinetic energy greater than threshold. The threshold energy is related to

	Argon	Oxygen	Nitrogen
Argon	1	0.816	0.768
Lead	0.542	0.266	0.237
Nitrogen	0.769	0.996	1
Oxygen	0.817	1	0.995
Selenium	0.892	0.559	0.511
Silicon	0.970	0.924	0.888
Tellurium	0.726	0.395	0.356
Titanium	0.992	0.750	0.700
Yttrium	0.856	0.516	0.470
Zinc	0.942	0.631	0.581

Table 2.4: Percentage of energy transfer between target and gas atoms.

the surface binding energy  $E_b^s$  as:

$$E_{th} = \frac{E_b^s}{\gamma(1-\gamma)} \tag{2.14}$$

if  $m_i/m_t < 0.3$ . Otherwise, the threshold energy is equal to:

$$E_{th} = 8E_b^s (\frac{m_i}{m_t})^{2/5} \tag{2.15}$$

and the surface binding energy values of the targets used in this work are given in Table 2.5.

Given the kinetic energy is sufficient, there are two different ways a target atom can sputter away from the surface. These ways are shown in Figure 2.6. It is not possible for a target atom to eject from a primary collision. Either the incoming ion can hit a target atom (atom A) and cause a collision with a neighboring target atom (target B) to provide it enough energy to be removed. Otherwise, the ion can hit a target atom and

Atom	Surface Binding
	Energy $(eV)$
Lead	2.02
Nitrogen	2.00
Oxygen	2.00
Selenium	2.14
Silicon	4.70
Tellurium	2.02
Titanium	4.89
Yttrium	4.24
Zinc	1.39

Table 2.5: Surface binding energy values

its remaining energy causes it to hit another target atom (atom C) that ejects from the surface. The response of the target atom depends on energy of the incoming ion and mass and atomic number of both the target atom and ion. There are five different responses.

- Ions will reflect off the surface and become neutralized in the process.
- Impact causes secondary ejection, as described earlier.
- Ion becomes buried in the target.
- Ion impact causes structural rearrangements inside the target.
- A series of collisions between atoms of the target occurs, which may lead to ejection of target atoms.



Figure 2.6: Collision cascade for target atoms removed from the target surface. This shows two possibilities with the ejection of either target atom B or target atom C.

### 2.3.4 Sputtering Mechanisms

Within the target, there are three sputtering mechanisms, shown in Figure 2.7, for ionbombardment that can occur depending on the amount of incoming energy. Single knockon occurs at very low energies. The first atom is hit by the incident ion and will absorb most of the energy. In general, the energy transfer is insufficient to cause sputtering. Instead the collisions cause only minor adjustments or corrections to the target. One way to utilize this is for smoothing out the target surface. Another mechanism is linear cascade, which occurs at intermediate energies. Most of the collisions involve only one moving and one stationary particle with very few number of recoils. Finally, the last type of sputtering is spike. This happens for very high energies where a large number of collisions occur between neighboring atoms. Second and third layer atoms are more likely to be sputtered off and the sputtering yield is very high. This large amount of energy can cause a surge in the thermal properties of the target, which leads to non-uniformity of the target material.



Figure 2.7: Types of sputtering mechanisms: single-knock on, linear, and spike. The type of mechanism depends on the energy of the incoming ion and can lead to several different structural properties of the material.

The choice of which sputtering mechanism to use largely depends on the objective. The advantage to linear cascade compared to single knock-on is that higher sputtering yields are achieved. For certain situations, the problem with this is that the collisions are mainly nuclear which lead to a higher probability of lattice disorder and amorphous films. In general, nuclear collisions typically occur when the ions have high kinetic energies, while electronic collisions typically occur at low kinetic energies(5). The probability of a nuclear collision can be quantified by its cross-section given by:

$$S_n(E) = 18.1a Z_1 Z_2 \frac{M_1}{M_1 + M_2} \left[\frac{\lambda_m}{2(1-m)} \varepsilon^{1-2m}\right]$$
(2.16)

$$a = \frac{0.0469}{\sqrt{Z_1^{2/3} + Z_2^{2/3}}} \tag{2.17}$$

$$\varepsilon = \frac{0.69a}{Z_1 Z_2} \frac{M_2}{M_1 + M_2} E \tag{2.18}$$

where  $Z_1$ ,  $Z_2$ , and  $M_1$ ,  $M_2$  are the charge and mass of the incoming ion and the target atom and  $\lambda_m$  and m are constants.  $\lambda_m$  is the Molier screen function, used to account for interactions between ions and atoms separated at any distance, and m is the power law parameter. Good values to use for IBSD are  $\lambda_m = 3.07$  and m = 0.216. So, the incoming energy must be carefully accounted for, especially for heavier targets such as PbTe and  $Y_2O_3$ . These have a higher probability of nuclear collisions and low energy threshold values. To avoid this unwanted change in crystal structure, the energy that corresponds to the lowest cross-section, but greater than  $E_{th}$  is desired. This means that materials such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> only have a small window of compromise between being able to achieve good crystalline quality while still sputtering off the material.

Spike sputtering mechanism is advantageous because of its high sputtering yield, but can lead to an unwanted thermal surge in the target material. The magnitude of the thermal surge is related to the stopping power. The stopping power is the rate of energy loss per unit distance traveled within the target material, and is equal to the nuclear stopping cross-section multiplied by the density of the target source. For a target material with heavier atoms and higher density, the incoming ion does not travel a significant depth. Therefore, light materials will have a lower threshold for spike collisions to occur, where targets like PbTe will not. This explains why lower beam currents and beam voltages were used for PbTe.

#### 2.3.5 Target to Substrate

After the atoms are sputtered from the target, they travel to the substrate. During their travel, many inelastic collisions will occur with other particles in the plasma. This leads to a reduced energy loss by the time the target atom reaches the substrate. The average energy loss of an atom that has been sputtered from the target, assuming travel only through argon gas plasma, can be given by(6):

$$E_F = (E_0 - k_b T_{Ar}) exp[\frac{dP\sigma}{k_b T_{Ar}} ln(E_f/E_i)] + k_b T_{Ar}$$
(2.19)

where d equals the distance traveled, P is the sputtering gas pressure,  $\sigma$  is the collision cross-section, and T is temperature of the sputtering gas. Since the distance traveled is fixed within the given system, the average energy loss is mainly affected by the chamber pressure and temperatures.

The collisions that the atom undergoes when traveling from target to substrate could lead to inability of the the atom reaching the substrate. One way to classify the sputtering process is through its efficiency, also known as the sputtering yield. The yield can be found as the ratio of the number of emitted ions from the RF source to the number of incident target atoms(7).

$$Y(E,\beta) \approx \frac{4.2\alpha(\beta)S_n(E)}{E_b^s}$$
(2.20)

where  $\alpha(\beta)$  is a constant related to the angle of incidence  $\beta$ ,  $S_n(E)$  is the nuclear stopping cross-section from Eq. 2.16, and  $E_b^s$  is the surface binding energy. For a compound target material, the sputtering yield is calculated as(8):

$$Y^{A_x B_y} = \frac{x}{x+y} Y_A + \frac{y}{x+y} Y_B$$
(2.21)

where x is the composition of atom A and y is the composition of atom B.

Along with the average loss of energy and efficiency, the beam intensity of the atoms from the target is just as important. It follows the cosine law as:

$$J_{\Omega} = \frac{Y z^+ \delta A \cos \theta}{\pi} \tag{2.22}$$

where  $Yz^+$  is the total flux coming from the target source and  $\theta$  is the angle of deviation from the target.  $Yz^+$  can be calculated from the sputtering yield, given in Eq. 2.20 and average energy loss from Eq. 2.19. Note that this equation is ideal and ignores the charge exchange that occurs in the target sheath. The number of collisions that occur in the target sheath due to charge exchange would reduce the flux and potentially the angle of deviation.

#### 2.3.6 Substrate Surface

The number of atoms reaching the substrate is different from the number of atoms emitted from the target. There are four contributing factors: target-to-substrate angle flux  $j_i$ , flux from the plasma power  $j_{part}$ , flux due to condensation  $j_{thermo}$ , and flux contribution dependent on the kinetic energy of the atoms  $j_{sput}$ . The total beam flux is then found by summing up each contribution  $j_{total} = j_i + j_{part} + j_{thermo} + j_{sput}$ , and the individual factors are equal to:

$$j_i = \frac{J_\Omega \cos\beta}{R^2} \tag{2.23}$$

$$j_{part} = \frac{3kT^{-}}{2(-q)}j_{e} + (V_{p} - v_{sub})j_{ion} + \frac{E_{i}}{q}j_{ion}$$
(2.24)

$$j_{thermo} = \frac{\Delta_{cond}H}{N_a} \alpha j_i \tag{2.25}$$

$$j_{sput} = \frac{E_s^2}{2} \delta j_i \tag{2.26}$$

This is a very simplified model, and a more accurate model that accounts for random collision can be found in Ref. (6).

The total beam flux can become quite large, and this typically leads to induced heating at the substrate surface. This is one disadvantage of the IBSD system, and further details are provided in Section 7.7.1. The rate of temperature increase can be determined by:

$$\Delta T = \frac{j_{total}}{\rho \omega C} \tag{2.27}$$

where  $\rho$  is the density of the substrate,  $\omega$  is the substrate thickness, and C is the specific heat of the substrate. Values of temperature increase at the surface due to the beam flux has been reported to be anywhere between 50 °C(9) to 100°C(10).

## 2.4 Comparison of Deposition Techniques

There are a number of different thin-film techniques varying from chemical techniques including dip coating, thermal oxidation, and CVD, to physical techniques from PLD, ion-assisted evaporation, ion-plating, EBE, and IBSD. One of the major advantages common to all CVD techniques is the ability to achieve high crystalline quality, but this typically comes at the cost of requiring high substrate temperatures which may not be suitable for temperature-sensitive applications (9). Since CVD does not work on the principle of elastic collisions, this generally results in less induced damage, better conformal coverage(11), and lower operating expenses since a high vacuum chamber is not required. Dip coating has many advantages including low costs and simplicity. This technique is versatile with the material selection, being capable of coating a very large surface. The production rate can be very high and high temperatures are not required, making this technique suitable for applications where material quality is not detrimental. Some of the disadvantages to dip coating include being messy, hazardous, and having limited controllability. Thermal oxidation is a good technique when accurate control of layer thicknesses is required. Further, it is advantageous when growing on multiple wafers at a time. Some of the disadvantages to oxidation include the limitation in choice of substrates used, and the interface quality between the thermally formed oxide and the substrate. The PECVD system has more advantages compared to the others in many ways including very fast deposition times. However, its main disadvantages are the high substrate temperatures and residual inhomogeneities (12)(13)

Physical vapor deposition techniques are good for applications that require versatility, especially in the type of source that can be used. Due to the way the materials are formed and adhere to the substrate, there tends to be more flexibility in the material properties. High quality materials can be achieved from control in the contamination within the high vacuum chamber, but this tends to come at the cost of other factors. PLD is a good technique when requiring stoichiometric and crystalline materials. The deposition rates are fast and virtually any material source can be used. Further, the technique is scalable and flexible with ease in maintenance due to isolation of the laser source from the chamber. However, disadvantages include unwanted particulate deposition and high defect rates, in addition to non-uniform deposition and uneven conformal coverage. Ion plating, ion-assisted deposition, and ion-beam evaporation are all three similar techniques with only slight differences in their physical operation. These techniques are simple and quick with affordable operating costs and maintenance expenses compared to the other PVD system. The main disadvantages are with the material quality, resulting in films that tend to be rough and porous. This is due to the evaporation mechanism where the material can be melted unevenly leading to instabilities in film growth and the geometry of the system can lead to poor uniformity. The compound materials can evaporate in a random fashion, which leads to differences in vapor composition due to molecular charge changes and material decomposition with variations due to beam curling effects. Finally, the last PVD technique is IBSD which can be very good in achieving high density and smooth surfaces. Unlike PLD or EBE, this system does not require high substrate temperatures in order to achieve this and the range of achievable material characteristics is rather large.

The flexibility of the IBSD system can lead to good repeatability, uniformity, thermal stability, control of stress(14), control with the growth orientation(15), and excellent electrical properties(16). This flexibility can be attributed due to the utilization of a secondary ion source that provides improved stoichiometry and enhanced grain growth, but the system can become complex with many tradeoffs in properties. Further, the high-energy ion bombardment can lead to unwanted surface damage; an issue further addressed in Section 8.4.2. Another issue with the films by IBSD is the large amount of compressive stress. The contribution to the compressive stress is the small spacing between grains in dense films. As the grains become closer and closer, they begin to repel and create a local compressive stress(14). The causes and solutions to this problem are discussed in Section 6.1.2.

The results achieved in this work were done with an IBSD and the reason for this choice is due to its advantages for the targeted applications. This section provides a comparison of the IBSD to two other commonly-used techniques: PECVD and EBE. Table 2.6 provides a summary of the comparison and the side-by-side characterization results are given in Section 2.4.1, 2.4.2, and 2.4.3. The properties of the films vary greatly depending on the deposition technique, parameters, and conditions, so the comparison provided here was done with optimized conditions of SiO<sub>2</sub> for the targeted objective of high density, low absorption materials. Different conditions would be necessary for a different targeted objective.

	Advantages	Disadvantages
$\begin{array}{c} \text{EBE} \\ \text{Al}_2\text{O}_3 \\ \text{Y}_2\text{O}_3 \\ \text{SiO}_2 \\ \text{TiO}_2 \end{array}$	<ul> <li>Median deposition times</li> <li>Simple and easy to use</li> <li>Ability to use any material</li> <li>Affordable cost and operating expenses</li> <li>Improved film composition by using a reactive gas</li> </ul>	<ul> <li>Deposits films that are very porous and have a columnar microstructure</li> <li>Uneven melting of the material</li> <li>Compound materials evaporate causing instabilities in molecular charge resulting in different vapor composition</li> <li>Poor uniformity</li> <li>Material decomposition due to heating</li> <li>Large variations in the deposition rate due to beam curling</li> </ul>
PECVD SiO <sub>2</sub> SiN	<ul> <li>Fast and short deposition times</li> <li>Good conformal coverage</li> <li>High vacuum not required</li> <li>Low cost and operating expenses</li> <li>Ability to achieve high-quality stoichiometric films</li> </ul>	<ul> <li>High substrate temperatures required</li> <li>Large amount of bond strain in films</li> <li>Limited number of materials</li> <li>Large edge effect on the sample from the plasma sheath</li> </ul>
IBSD Ge GeO <sub>2</sub> PbTe SiO <sub>2</sub> Si <sub>3</sub> N <sub>4</sub> SiO <sub>x</sub> N <sub>y</sub> Ti TiO <sub>2</sub> TiN ZnO ZnSe	<ul> <li>Ability to use any material</li> <li>No target material decomposition</li> <li>Resputtering achieves dense, high-quality films</li> <li>Can effectively modify the film stress and adhesion</li> <li>Able to deposit films in different crystallographic orientations</li> <li>Flexibility due to independent control of sources</li> <li>Excellent uniformity and repeatability</li> <li>Secondary assistance source allows for smooth surfaces and good grain growth</li> <li>Secondary assistance source compensates to achieve stoichiometric films</li> <li>High energy target atoms leads to more densely packed films</li> <li>Low amount of contamination and water in films due to high vacuum chamber</li> </ul>	<ul> <li>High vacuum required leading to more expensive costs</li> <li>Long deposition times</li> <li>Surface susceptible to damage from high energy ion bombardment ion bombardment</li> <li>Higher chance of interfacial mixing</li> </ul>

Table 2.6: Summary of the comparison of EBE, PECVD, and IBSD listing the advantages, disadvantages, and available materials.

-

### 2.4.1 Structural Properties

Figure 2.8 shows the scans of the surface morphology of the three samples by AFM. The surface morphology is important for reduced light scattering and low amounts of light loss. The measured RMS roughness values were 1.050 nm for EBE, 1.291 nm for PECVD, and 0.334 nm for IBSD. The average grain profile is shown in Figure 2.9, with sizes of 23.5 nm<sup>2</sup> for EBE, 21.2 nm<sup>2</sup> for PECVD, and 3.1 nm<sup>2</sup> for IBSD. The EBE sample exhibits large spikes and odd shapes with its grain cross-section. The PECVD sample grain cross-section shows an unwanted shoulder peak, and this can be attributed to due to coalescence. Finally, the IBSD sample shows a grain that is very small and symmetrically shaped.



Figure 2.8: Comparison of AFM scans of  $SiO_2$  by EBE, PECVD, and IBSD. Measured RMS roughness values were 1.050 nm for EBE, 1.291 nm for PECVD, and 0.334 nm for IBSD

To compare the relative packing density of the films, the chemical acid etch rate can be used in conjunction with the behavior of the absorption bands. In general, a more densely packed film will have less voids and air/water between grains, and will therefore have a lower etch rate whereas a porous film will be etched away more quickly. All three



Figure 2.9: Cross-section of the grain profiles of the three  $SiO_2$  samples extracted from the AFM scan. The average grain sizes were 23.5 nm<sup>2</sup> for EBE  $SiO_2$ , 21.2 nm<sup>2</sup> for PECVD  $SiO_2$ , and 3.1 nm<sup>2</sup> for IBSD  $SiO_2$ 

samples were simultaneously immersed in undiluted buffered HF acid for 15 seconds. The etch rates were EBE = 57.76 nm/sec, PECVD = 39.15 nm/sec, and IBSD = 1.71 nm/sec. In addition to faster etching rates, the amount of lateral undercut was significantly worse for the EBE and PECVD sample. Patterning each sample with a 5  $\mu$ m opening, the lateral undercut was 2.16  $\mu$ m for EBE, 0.94  $\mu$ m for PECVD, and 0.16  $\mu$ m for IBSD on each side.

### 2.4.2 Electrical Properties

Comparing the electrical properties was done by measuring the C-V curves of MIS capacitors. The C-V measurements are shown in Figure 2.10, and the procedure is discussed in Section 3.2.2. The C-V curve for the MIS capacitor with  $SiO_2$  by EBE was omitted because of erroneous curves. This problem may be due to the large amount of porosity in the films.



Figure 2.10: Normalized C-V measurements of two MIS capacitors using SiO<sub>2</sub> by PECVD and IBSD taken at a frequency of 1 MHz. The samples had a difference in flatband voltage of  $V_{FB} = 7.820$  V, fixed oxide charge of  $Q_f = 2.05 \times 10^9$  cm<sup>2</sup>, and density of interface traps  $D_{it} = 1.19 \times 10^8$  cm<sup>-2</sup> eV<sup>-1</sup>

The C-V curves were measured to compare the flatband voltage, density of fixed oxide charges, density of interface charges, and interfacial trap level density. The flatband voltages for both samples were negative values, indicating a positive fixed charge located in the dielectrics. A much higher positive fixed charge is seen in the PECVD SiO<sub>2</sub>, with a flatband voltage shift of  $V_{FB} = 7.05$  V. This results in a much larger density of fixed oxide charges with a difference of  $\Delta Q_f = 2.05 \times 10^9$  cm<sup>2</sup>. The density of interface charges were then compared with high and low frequency measurements. Both samples exhibited a stretchout, however the PECVD SiO<sub>2</sub> exhibited a larger stretch that is almost four times larger in magnitude. For PECVD SiO<sub>2</sub>, a change in its normalized capacitance of  $(\Delta C/C_{ox}) = 0.192$  occurred. Finally, the density of interface traps was larger in the PECVD SiO<sub>2</sub> with a difference of  $\Delta D_{it} = 1.19 \times 10^{-8} \text{ cm}^{-2} \text{ eV}^{-1}$ .

### 2.4.3 Optical Properties

The FTIR measured transmittance curves are provided in Figure 2.11. The optical curves were similar with a few differences due to the refractive indices and absorption. The dispersion curves of the refractive indices measured by ellipsometry are shown in Figure 2.12. The refractive index values were around n = 1.39 for EBE SiO<sub>2</sub>, n = 1.42 for PECVD SiO<sub>2</sub>, and n = 1.44 for IBSD SiO<sub>2</sub>. The lower refractive indices are most likely due to the number of pores in the films that are filled with either air ( $n \sim 1$ ) or water ( $n \sim 1.33$ ).

The absorption coefficient curves are provided in Figure 2.13. The water absorption band is due to the presence of silanol groups and water(17). The second absorption band is a sharp, but weak band located around  $\lambda \sim 4.25 \ \mu\text{m}$  in the IBSD SiO<sub>2</sub> and is due to a small amount of CO<sub>2</sub> present in the chamber that can backflow into the primary deposition ion source(18). The third absorption band is due to Si-O stretching vibrations. This is present in all samples and is characteristic to the SiO<sub>2</sub> fingerprint. The EBE sample had the largest peak with  $\alpha = 6472 \text{ cm}^{-1}$  and a FWHM of 1.11  $\mu\text{m}$  at 9.3  $\mu\text{m}$ . For the PECVD peak,  $\alpha = 4851 \text{ cm}^{-1}$  and a FWHM of 1.14  $\mu\text{m}$  at 9.25  $\mu\text{m}$ , and for the IBSD sample,  $\alpha$ = 4510 cm<sup>-1</sup> and a FWHM of 1.11  $\mu\text{m}$  at 9.17  $\mu\text{m}$ . There is also a shoulder exhibited at 10.5  $\mu\text{m}$  with the EBE sample, also due to Si-O stretching vibrations. The fourth



Figure 2.11: FTIR measured transmittance of  $SiO_2$  by EBE, PECVD, and IBSD

and fifth absorption bands are due to bond-bending located at 12.4  $\mu$ m and bock-rocking located around 22  $\mu$ m. All samples had these bands present in their curves with only small differences in intensity.

To determine the porosity of a film, its etch rate should be used in combination with shifts in the absorption bands. A more densely packed film will have its stretching band shift to shorter wavelengths and bending band shift towards longer wavelengths(19)(20). The shift can be explained due to the bond strength k, give in Eq. 7.7, which affects both the stretching and bending. Further, the magnitude of porosity can be calculated using the water band(21):

$$1 - P_f = \frac{\beta_{PECVD} - \beta_W P_W}{\beta_{IBSD} - P_W}$$
(2.28)



Figure 2.12: Refractive indices of SiO<sub>2</sub> by EBE, PECVD, and IBSD measured by ellipsometry. Values at  $\lambda \sim 600$  nm were determined to be  $n^{EBE} = 1.39$ ,  $n^{PECVD} = 1.42$ , and  $n^{IBSD} = 1.44$ 

$$\beta_i = \frac{n_i^2 - 1}{n_i^2 + 2} \tag{2.29}$$

$$P_W = \frac{\ln(T_{IBSD}/T_{PECVD})}{\alpha d} \tag{2.30}$$

where  $n_W$  is the refractive index of water,  $n_{IBSD}$ ,  $T_{IBSD}$ , and  $n_{PECVD}$ ,  $T_{PECVD}$  are the refractive indices and measured transmittance of the samples,  $\alpha$  is the absorption coefficient value at the peak, and d is the film thickness. The IBSD SiO<sub>2</sub> was calculated to have a film density that is at least seven times higher than the PECVD SiO<sub>2</sub>. This difference in density means that the PECVD SiO<sub>2</sub> has approximately 86% more pores. This was confirmed using UV-NIR ellipsometry.



Figure 2.13: Plot of the absorption coefficient of  $SiO_2$  by EBE, PECVD, and IBSD. This information can be used not only to determine the loss of light intensity, but also the porosity of the films with observation of the shift in Si-O bands and intensity of the water band.

# **CHAPTER 3**

# Material Characterization

The properties and behavior of the thin-film dielectrics can be fully understood by using a series of characterization techniques. This chapter provides the background and overview of the characterization tools used in this work. First, the structural properties are characterized using SEM, AFM, XRD, and chemical acid etching, as described in Section 3.1. As important as the structural properties are the electrical properties which were characterized using Hall or four-point probe measurements and capacitance-voltage measurements. The two are described in Section 3.2. Finally, some of the more important optical properties include refractive index and absorption coefficient of the materials. There are many different methods and tools that can be used, and some of them are discussed in Section

### 3.1 Structural Characterization

The structural properties are important in this work include surface morphology, high film density, low stress and strain, homogeneity, good adherence, and good interface quality. This section discusses how the different tools can be used to quantify these properties.

### 3.1.1 Atomic Force Microscope

Atomic force microscope (AFM) is a high-resolution instrument that measures that topography and morphology of a sample using the force of a probe. The force between a sharp tip and the sample surface is measured, and from this a 3D image of the surface contour can be created. In addition to determining the surface morphology, information such as height, size, and shape of the film or defects can be characterized for better understanding of the film nucleation. The system is also useful for understand the growth modes by analyzing the atomic steps seen with the characterization. Further, these scans can provide information on spacing between grains that can lead to light scattering and losses due to light trapping.

The AFM system consists of three main components. The first is a micro-scale cantilever with an attached small sharp tip. The cantilever tip is lowered in proximity to the sample surface. The tip scans the surface of the sample, and any force will then cause the cantilever to bend and move up or down along the contour of the surface. Second, a laser shines a spot onto the cantilever and its reflected light is measured by the third major component, the detector. Any change in reflection of the laser during the scan is measured with the detector and then converted to a voltage. The morphology of the surface causes small changes in the position of the cantilever that will tilt the reflected beam to change its position and intensity seen by the detector.

The three-dimensional presentation of the sample contour is accurate down to an order of microns in size. There are some advantages to the system including not requiring a vacuum, accessibility to certain regions which typically could not be accessed with STM, and non-destructive imaging. However, the tip is very sensitive making it prone to damage and the size of the tip can lead to image misrepresentation with any surface feature larger than it.

### 3.1.2 Scanning Electron Microscope

Scanning electron microscope (SEM) is a powerful tool, similar to an optical microscope but different in that it uses electrons instead of light waves to produce a high-resolution 3D image. Information that can be obtained from SEM includes layer thickness, surface morphology, interface quality, defect imaging, and microstructure or stress. Also, the system has been typically used to check the conformal coverage and cross-sectional shape.

There are three main components used in the system: electron gun, control console, and a vacuum system. There are many different types of electrons that can be used such as a thermionic field emitter, thermal field emitter, or schottky emitter. The operation of the system is as follows. An electron beam is directed along a vertical path through a microscope and focused by lenses onto a small spot size. Pairs of scanning coils or deflector plates are used to deflect the beam horizontally and vertically to raster the specific area. Electrons are emitted from a cathode and accelerated towards the anode. It will interact with the sample, lose energy, and then become detected. The energy exchange that occurs between the electron beam and sample results in the emission of auger electrons, x-rays, and backscattered electrons.

One advantage to the SEM system is that 3D images can be viewed at a much higher magnification than optical microscope. It has a high degree of control, large depth of field, and requires less voltage than TEM. Furthermore, it is flexible in the different types of sample that can be characterized. One disadvantage to this technique is that the electrons produce only black and white images. Further, another setback with the system is that the samples must be conductive and stable under vacuum in order to obtain accurate imaging. So, this can become difficult in characterizing the dielectrics, especially when observing layers less than about 100 nm.

### 3.1.3 X-ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique that uses the scattered intensity of x-rays to determine the crystallographic structure, chemical composition, and physical properties. From the XRD characterization results, information such as chemical composition, crystallographic structure, film stress/strain, and density can be characterized. The diffraction pattern can then be used to determine information about the distribution of the atoms in the material. A perfectly periodic crystal will lead to sharp interference peaks with the same symmetry as the atoms.

The x-ray source is focused onto the sample and x-ray photons will collide with the

distribution of electrons within the material. This causes a deflection away in a different direction that will become detected. The diffracted waves from the different atoms can interfere with each other, and this leads to a change in the intensity distribution.

XRD is a very powerful technique that can lead to a lot of information about the material. One useful piece of information that can be extracted is the grain size of the microstructure(22).

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{3.1}$$

where  $\lambda$  is the x-ray wavelength, B is the FWHM of the x-ray peak, and  $\theta$  is the Bragg angle. Another important property that can be extracted is the film stress. The film stress of two films can be relatively compared by finding any changes in interplanar spacing. The amount of film contraction that occurs in the xy plane is given as(23):

$$\sigma_f = -\frac{Y(a-a_0)}{2va_0} \tag{3.2}$$

where Y is young's modulus, a is the measured lattice parameter, and  $a_0$  is the bulk lattice parameter.

### 3.1.4 Chemical Acid Etching

One way to characterize the density of films is by etching in a chemical acid. In general, a more porous film will have a higher etch rate. The density of the material also affects any selective etching that occurs. For example, a solution of HF:HNO<sub>3</sub>:H<sub>2</sub>O in ratios of around 10:10:450 can be used to selectively etch SiO<sub>2</sub>(24). The density of etch pits can be used to observe the void density in the material. In addition to etch rate and density of pits, the etch profile of a material is extremely important since the etch rate from the top to bottom can be different from the lateral undercut rate.

# 3.2 Electrical Characterization

The electrical properties that were important in this work include highly insulating, good dielectric constant, ideal flatband voltage values, controllable fixed oxide charge, and low density of interface states. This section discusses how both the Hall measurements and capacitance-voltage measurements can be used to determine whether this was achieved.

### 3.2.1 Hall and Four-Point Probe Measurements

Hall and four-point probe measurements quantify the electrical properties of films by using four probes to make contact with the top surface of a sample. A current I is applied between two of the probes and the voltage V is measured between the other two. From this, information such as the carrier concentration and mobility can be determined. Further, the sheet resistance is determined by the applied voltage and measured current as:

$$R_s = CF \times \left(\frac{\pi t}{\ln 2}\right) \times \left(\frac{V}{I}\right) \tag{3.3}$$

where t is the thickness of the film and CF is the correction factor. The correction factor can vary and this is related to the size and shape of the sample(25) (26). For four-point probe measurements in this work, samples were cleaved in a square shape into the smallest

size permissable. This typically meant sizes around 1 mm x 1 mm, and a corection factor value of 1 was used.

The advantage to using the four-point probe technique is that it is simple and the voltage probes are independent of the current probes. This isolation causes the Schottkly contact resistance to be negligible which alleviates some of the complicated calculations and inaccuracies. The Hall bar and four-point probe measurements are very similar, except that the Hall bar measurement involves an extra step of patterning the sample into a fixed feature. This makes Hall bar measurement a destructive characterization technique and involves a bit more complexity and preparation work, but the measurements results are more accurate due to preventative current spreading.

### 3.2.2 Capacitance-Voltage Measurements

Measurements of voltage dependent capacitance were done with metal-insulator- semiconductor (MIS) capacitors. Information such as dielectric constant, dielectric breakdown, fixed oxide charge, and interface trap level density can be found. Another property that can be measured is the flatband voltage, which is the voltage equal to the voltage across the insulator plus the surface potential. A non-zero surface potential will cause the energy bands to bend, and this is undesirable because of Fermi level pinning at the interface.

There are three main states that the capacitor can be in: accumulation, depletion, and inversion. The state the capacitor is in depends on the applied gate voltage  $V_G$  and the response of charges due to this bias. The general difference between the three states is the interactions of holes and electrons with the surface. Accumulation leads to the attraction of electrons at the surface whereas depletion is the attraction of holes and repulsion of electrons. Finally, inversion occurs when the density of exceeds the density of electrons in the bulk, leading to inversion of the surface.



Figure 3.1: Illustration of the four different charges in an insulator: mobile ionic, trapped oxide, fixed oxide, and interface trapped oxide.

The different types of factors that contribute to the measured results can make the analysis complicated by altering the capacitance value, shape, and behavior with respect to bias voltage, frequency, and sweeping direction. In all cases, charge neutrality must be maintained. This means that the charge due to the (a) gate voltage, (b) surface potential, and (c) interface traps must add up to be zero. So, it is important to determine how these three factors affect the C-V measurements.

The change in capacitance can be isolated by considering the four different charges, illustrated in Figure 3.1. These are: mobile ionic, trapped oxide, fixed oxide, and interface trapped. The main focus in this work will be with the fixed oxide charges and interface trapped charges. Ref. (27) can be used to find information on the other charges.

First will be a discussion on the fixed oxide charges. The effect of the surface potential

has on the C-V measurements are shown in Figure 3.2. Any non-zero surface potential will also lead to a non-zero flatband voltage. When there is a surface potential introduced, the result is a shift in the C-V curve by an amount equal to the flatband voltage. A shift towards more negative values means that the surface is positively charged, and any shifts towards more positive voltages means that the surface potential is more negatively charged. The difference in voltage from the shift in C-V is how the flatband voltage is determined.



Figure 3.2: Example plots of the capacitance change with bias voltage. The left hand figure shows a high frequency measurement compared to ideal, representing how the flatband voltage causes a shift in the curve. The right hand figure is a low frequency measurement compared to the high frequency measurement showing how the density of interface traps causes a stretchout in the curve. The stretchout can be quantified by looking at the slope of the curve in the depletion region.

Now that the fixed oxide charges have been considered, the interface trapped charges can be discussed. The effect of the density of interface traps on the C-V measurements is a stretchout of the C-V curve, as shown in Figure 3.2. The stretchout occurs between the low frequency curve and the high frequency curve. The low frequency is needed is in order to allow the charges the chance to respond in the depletion region. The stretchout occurs because the change in occupancy of the traps leads to energy losses, and as a result, driving the capacitor from accumulation to inversion requiring a larger change in gate voltage. Acceptor interface traps are negative when filled and neutral when empty, whereas donor interface traps are neutral when filled and positive when empty.

While the shift and stretchout of the C-V curve is very important, there are also a few other aspects of the curve that should be noted. One aspect is an observable hysteresis when sweeping from accumulation to inversion where charge trapping of electrons occur, and then back from inversion to accumulation where detrapping occurs. Also, the variation of the accumulation capacitance with different frequencies can occur due to the interface carriers having different response times. These issues can lead to instability of the electrical properties and should be considered.

### **3.3** Optical Characterization

For optoelectronic devices, the appropriate structures could not be developed without the knowledge of the material's refractive index, extinction coefficient, and bandgap. This information can be found here in this section.
### 3.3.1 Ellipsometry

One way to measure the optical properties of the films is by using ellipsometry. Ellipsometry is a non-destructive technique where polarized light can be used to determine the layer thickness, refractive index, extinction coefficient, and composition of the films. Elliptically polarized light occurs when two perpendicular waves with unequal amplitude combine, as shown in Figure 3.3. The amount of ellipticity is influenced by the optical constants and parameters of the film.

The ellipsometer system consists of many different components. The light beam is generated by the source and passes through a fixed input polarizer. A small amount of modulation is induced and then hits the sample surface. Light reflected off the sample passes through the analyzer and then to a monochromator. The purpose of the monochromator is to separate the light into an s-polarized wave and p-polarized wave, and to change the wavelength of light seen by the detector. The light must consist of both parts in order to form the elliptically polarized light, the s-polarized is oriented perpendicular and the p-polarized is oriented parallel to the plane.

The principle behind ellipsometry involves differences between the reflected s-polarized and p-polarized waves. The light hits the sample, and is then reflected undergoing a shift in phase of:

$$\Delta = \delta_1 - \delta_2 \tag{3.4}$$

where  $\delta_1$ ,  $\delta_2$  are the phase differences between the s-polarized and p-polarized waves before and after reflection. In addition to a change in phase, the reflected light undergoes



Figure 3.3: Illustration showing the formation of elliptically polarized light formed by two perpendicular waves of unequal amplitude.

a change in amplitude.

$$\Psi = \frac{|R^p|}{|R^s|} \tag{3.5}$$

Combining Eq. 3.5 and 3.6, the fundamental equation of ellipsometry is obtained (28):

$$\tan \Psi e^{i\Delta} = \frac{R^p}{R^s} \tag{3.6}$$

where  $\mathbb{R}^p$  and  $\mathbb{R}^s$  are the Fresnel reflection coefficients of the p- and s-waves.

$$n = \sqrt{\frac{1}{2} [\varepsilon_1^2 + \varepsilon_2^2]^{1/2} + \varepsilon_1}$$
(3.7)

 $\Delta$  and  $\Psi$  and complex models are then used to deduce the optical parameters of the

films. Instead of work with the refractive indices, these models work with the dielectric constant. The refractive index and extinction coefficient are computed as:

$$k = \sqrt{\frac{1}{2} [\varepsilon_1^2 + \varepsilon_2^2]^{1/2} - \varepsilon_1} \tag{3.8}$$

One caveat is that the fundamental equation of ellipsometry cannot be accurately inverted to achieve a solution to the optical parameters. Therefore, regression analysis and computer simulations must be used. The solution after each iteration is evaluated by using either the mean square error or the point-wise experimental error as a merit function(29). There exist many different models for this, and the appropriate choice depends on the type of structure and quality of the material. The model used for the measurements in this work was the effective medium approximation (EMA)(30), which attempts to seek the best average using an extensive amount of mathematics and a large number of iterations. A brief discussion on commonly used models is given in Ref. (29).

In addition to measuring the refractive index, the ellipsometer can be used to measure the bandgap of a material using the absorption curve separated into three different regions, as shown in Figure 3.4. Region 3 occurs when a large amount of excess photons are absorbed giving it enough energy to jump the bandgap. Therefore, those absorbed photons have an energy that is either near or greater than the bandgap energy. The absorption is dominated mainly by the incoming photon energy with values typically of  $\alpha > 10^4$  cm<sup>-1</sup>. In region 2, the absorption edge has broadened and this corresponds to the situation where the photons have just barely enough energy to be absorbed and the electrons are pushed to jump the bandgap. The absorption is mainly dominated by the energy of the electrons with values typically around  $\alpha \sim 1 - 10^4 \text{ cm}^{-1}$ . Finally, for low absorption levels  $(\alpha < 1 \text{ cm}^{-1})$ , the absorption is mainly due to the Urbach tail. The shape of the Urbach tail can vary and this depends on the purity and structure of the material.

In general, dielectrics with good insulating capabilities will have a low conduction due to its large bandgap. The energy states within the gap are expected to contain energy bands below the absorption edge or exhibit an absorption tail, and this is how the bandgap can be determined. The absorption edge is related to the photon energy by what is known as the  $E^2$  rule(31). The bandgap of the material is then related to the absorption edge using Tauc's law(32):

$$\sqrt{\alpha\hbar\omega} = A(\hbar\omega - E_g) \tag{3.9}$$

where A is a characteristic parameter. Using this equation, the optical bandgap of the film material is found by linear extrapolation to  $(\alpha \hbar \omega)^2 = 0$ .

Finally, the last parameter the system can measure is the thickness of the films using the ellipsometric angles. The thickness is measured by observing the  $\Delta/\Psi$  trajectory, and then the thickness is extracted from where the trajectory closes on itself.

$$d = \frac{\lambda}{2\sqrt{n_2^2 - n_1^2 \sin^2 \phi}} \tag{3.10}$$

where  $\phi$  is the angle of the incoming light normal to the surface,  $n_2$  is the refractive index of the film,  $n_1$  is the refractive index of air, and  $\lambda$  is the wavelength of the monochromator.



Figure 3.4: Separation of the near-band edge absorption curve into three different regions needed to use Tauc's law given in Eq. 3.9.

# 3.3.2 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is a non-destructive, analytical method used to obtain the spectra of a sample through the detection of vibrational characteristics. With the interaction of incident light, the chemical bonds in the sample may change by stretching, contracting, or bending. This results in the absorption of incident radiation occurring at a specific wavenumber.

The system has four main components. There is a HeNe laser, and its purpose is to be the master clock of the system and count the sample collection in wavenumbers. The system is equipped with multiple mirrors with two located at the vertex of a 45° angle relative to the beamsplitter. There is a broadband light source that is split into two parts one hitting each mirror. The light travels back to the interferometer with a phase difference, and this are how an interference pattern, called an interferogram, is formed. The interferogram signal transmits or reflects light off the sample surface and the interaction of the signal is then measured by the detector. The detected interferogram cannot be directly interpreted, so it is decoded using the Fourier transform(33).

The absorbance is found by taking the ratio of the intensity with the sample in the beam path to the intensity of the measured background. Then the transmittance or reflectance is related to the absorbance as:

$$A = \log_{10}(1/T) \tag{3.11}$$

For the transmission measurements, the background was air, and for reflectance measurements, the background was a gold-covered glass slide.

#### 3.3.3 Refractive Index and Absorption Calculations

The refractive index and absorption coefficient are very important optical parameters that describe the behavior that light will experience when traveling through a particular material. This information is needed in many applications, especially for optical improvements. For this work, a direct measurement of these two optical parameters was not available. As a result, the parameters were extracted from theoretical fitting to the experimental FTIR measured spectra. There are many different models that can be used to extract this information (34)(35)(36)(37)(38)(39)(40)(41)(42), and each one is suitable for different types of structures, material properties and characterization tools. Since there are so many different ways to extract this information, the methods and calculations used for this work is given here.

First, information on the substrate is needed, and can be done so by using a quick estimation of  $n_s = T_s^{-1} + [T_s^{-2} - 1] - 1$  where  $T_s$  is the measured transmittance of the substrate(38). Figures B.1, B.2, and B.3 provide plots of the measured transmittance of the Si, ING, and Gabs substrates. A simple way to determine the optical constants is by using the maximum  $T_{max}$  and minimum  $T_{min}$  envelope of the measured transmittance curves. From this information, the refractive index can be determined as(37):

$$n = \sqrt{N \pm [N^2 - n_0^2 n_s^2]^{1/2}}$$
(3.12)

$$N = \frac{1}{2}(n_0^2 + n_s^2) + 2n_0 n_s \frac{\pm T_{max} \mp T_{min}}{T_{max} T_{min}}$$
(3.13)

and the absorption coefficient can be found as:

$$\alpha = \frac{(n+n_0)^2 [\pm 1 \mp \sqrt{T_{max}/T_{min}}]}{(n-n_0)^2 (n+n_s)^2 [1 + \sqrt{T_{max}/T_{min}}]}$$
(3.14)

where  $n_0$  is the refractive index of air,  $n_s$  is the refractive index of the substrate, and the choice of polarity used in the equations depends on whether  $n > n_s$  or  $n < n_s$ . There are many other ways this information can be extracted(43). However, one problem with these methods is the restriction that it will only work for very thick layers. Further, other techniques should be used for different types of films, for example films that are highly absorbing(44). In addition to absorption and thick films, one problem that can arise is ambiguity(45)(46)(47).

The ambiguity issue was avoided by using using two equations:

$$\frac{1+R}{T} = \frac{1}{4n_0 n_s A} [\chi_1 B \cosh 2\rho + 2C \sinh 2\rho + \chi_2 D \cos 2\gamma + 2E \sin 2\gamma]$$
(3.15)

$$\frac{1-R}{T} = \frac{1}{2n_s A} [n_f B \sinh 2\rho + 2C \cosh 2\rho + k_f D \sin 2\gamma - 2E \cos 2\gamma]$$
(3.16)

where  $A = n_f^2 + k_f^2$ ,  $B = n_f^2 + n_s^2 + k_f^2 + k_s^2$ ,  $C = n_f n_s + k_f k_s$ ,  $D = 2n_f k_s - n_f k_s$ ,  $\chi_1 = n_0^2 + n_f^2 + k_f^2$ , and  $\chi_2 = n_0^2 - n_f^2 - k_f^2$ . Finally, refinement of the results are done so with the first-order equations(48):

$$M = 2n_f^2 n_s \left[ 2\left(\frac{1+R}{T}\right) - \left(\frac{C_1}{C_2}\right) \left(\frac{1-R-T}{T}\right) \right]$$
(3.17)

$$M' = (1 + n_f^2)(n_f^2 + n_s^2) + (1 - n_f)^2(n_s^2 - n_f^2)\cos 2\beta$$
(3.18)

where the phase shift change is accounted for in the constants:

$$C_1 = 2n_s [2\beta(1+n_f^2) - \sin 2\beta(1-n_s^2)]$$
(3.19)

using the phase change

$$C_2 = 2\gamma (n_f^2 + n_s^2) + \sin 2\beta (n_s^2 - n_f^2)$$
(3.20)

Different values of  $n_f$  are attempted until the minimal difference between Eq. 3.17 and 3.18 is found. Once an appropriate  $n_f$  is found, the extinction coefficient is then calculated as:

$$k_f = \frac{2n_f^2 n_s}{C_2} \frac{1 - R - T}{T}$$
(3.21)

The calculated optical curves should be compared to the measured curves to verify the accuracy of the optical parameters obtained. Iterations are performed with slight variations in the initial  $n_f$  and the calculations are continually repeated until the correct solution is found. This process only calculates the indices of refraction for one given wavelength, and therefore must be repeated for all wavelengths of interest. One last verification is performed by matching up the refractive index from ellipsometry in the near-IR to the FTIR value(49). Further, the calculations may need slight adjustments due to complicated interference fringes and multiple internal reflections from rough surfaces, large thickness values, and inhomogeneous materials(35). This can be done by taking a second set of FTIR measurements performed with a high resolution. An example plot of the measurements of SiO<sub>2</sub> is given in Figure 3.5 shows the presence of interference fringes. The calculations necessary can be done so by using the information from the maximum and minimum envelopes of the high-resolution measurements, as shown in the plot.

Once a good match is found, the refractive index can be fitted to either the Cauchy or Sellmeier equation, as was done in Chapter 4. Both equations relate the dispersion of the refractive index with wavelength. The Cauchy equation is(50):

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(3.22)



Figure 3.5: High resolution FTIR measured transmittance of a  $SiO_2$  sample demonstrating the presence of interference fringes accompanied by plots of the maximum and minimum envelopes.

and the Sellmeier equation is(51):

$$n^{2}(\lambda) = 1 + \frac{B_{1}\lambda^{2}}{\lambda^{2} - C_{1}} + \frac{B_{2}\lambda^{2}}{\lambda^{2} - C_{2}} + \frac{B_{3}\lambda^{2}}{\lambda^{2} - C_{3}}$$
(3.23)

### 3.3.4 Optical and Linear Expansion Coefficient

When a film is exposed to a temperature changes, its optical and physical properties change. The refractive index undergoes a change due to the thermal optical expansion and the thickness undergoes a change due to the thermal linear expansion. Measurements of the thermal linear expansion can be formed using techniques such as XRD, discussed in Section 3.1.3. However, this works well with bulk materials, and the complexity and accuracy of the measurements becomes limited with thin films. The thermal optical expansion is necessary for applications such as the AR coatings because any optical expansion can lead to changes in the refractive index. Further, since it is desirable to use amorphous material for AR coatings to minimize the amount of light scattering, this makes XRD an impractical solution. This subsection provides a technique to use FTIR for the simultaneous measurement of the thermal optical and thermal linear expansion coefficients.

When a material is exposed to a change in temperature of  $\Delta T = T_0 - T$ , changes also occur in the reflectance and phase change(52). The overall reflectance spectrum can be measured for the two different temperatures  $T_0$  and T, and an expected change should be observed as:

$$R(T) = \frac{(r_1 + \Delta r_1)^2 + (r_2 + \Delta r_2)^2 + 2(r_1 + \Delta r_1)(r_2 + \Delta r_2)\cos(\delta + \Delta\delta)}{1 + (r_1 + \Delta r_1)^2 + (r_2 + \Delta r_2)^2 + 2(r_1 + \Delta r_1)(r_2 + \Delta r_2)\cos(\delta + \Delta\delta)}$$
(3.24)

For a single layer material on substrate, the reflectance at the film-substrate interface will change by an amount

$$\Delta r_1 = \frac{2n_f n_s}{(n_f + n_s)^2} \left[\frac{1}{n_s} \frac{dn_s}{dT} - \frac{1}{n_f} \frac{dn_f}{dT}\right] \Delta T$$
(3.25)

Further the reflectance at the film-air interface will change by an amount

$$\Delta r_2 = \frac{2}{(n_f + 1)^2} \frac{dn_f}{dT} \Delta T \tag{3.26}$$

Finally, the last change is with the phase difference, given by

$$\Delta \delta = \frac{4\pi nd}{\lambda} \frac{dn_f}{dT} + \frac{1}{t} \frac{dt}{dT}$$
(3.27)

where t is the film thickness. From these three equations, the thermal optical expansion  $dn_f/dT$  and the thermal linear expansion dt/dT can be determined. If the measured reflectance spectrum shifts towards longer wavelengths, then  $dn_f/dT > 0$ , and if the spectrum shifts towards shorter wavelengths then  $dn_f/dT < 0$ . Figure 3.6 shows an example change in the reflectance curve due to both thermal linear and optical expansion.



Figure 3.6: Reflectance of a  $SiO_2$  sample measured with FTIR at three different temperatures, showing shifts in both position and intensity due to thermal and optical linear expansion. The shift to a different wavelength is due to thermal expansion, whereas the shift to different reflectance value is due to optical expansion.

# 3.3.5 Photoluminescence

Photoluminescence (PL) is a non-destructive, optical technique that uses radiation to determine the properties of the film and/or interface. The incident radiation is absorbed giving the material excess energy. The excess energy causes the creation of electron-hole pairs, and therefore leads to radiative recombination photon emission. One use for PL is to determine the density of surface states because their presence will cause excess energy to be transferred to non-radiative recombination. Examples of PL measurements are given in Figure 3.7.

The PL setup consists of a laser, mirrors, filters, and a monochromator. Some of the advantages of PL include being a non-destructive and a contact-less technique. In addition, it is very sensitive and can be very accurate. However, this also means that it is sensitive to any unintentional dust or contaminants on the surface.



Figure 3.7: PL measurements from  $SiO_2$  on ING showing (a) an image from topographical PL showing a two-dimensional mapping of the surface defects and (b) a decrease in intensity of the substrate peak due to a change in the amount of non-radiative recombination.

# **CHAPTER 4**

# **Dielectric Materials**

This chapter provides the properties of seven different materials that were used in this work. The choice of materials depended on a number of different factors. Each material has its own unique advantages and disadvantages. Table 4.1 lists some of the major advantages and disadvantages of the seven materials, along with a few examples of applications. Then with the entire set of all seven, the hypotheses proposed in Chapter 7 and Chapter 8 can be explored. Ranges of achievable structural, electrical, and optical properties are provided here. In addition, solutions for the listed disadvantages are provided.

# 4.1 Lead Telluride (PbTe)

Lead telluride is not a material that is typically used like the other dielectrics discussed in this chapter. It is useful because of being a low-absorbing material in the IR with very high refractive index. One particular application is optical coatings for optoelectronic devices(53), such as lasers and detectors. Further, PbTe has potential as being used a

Advantages	Disadvantages	Applications
PbTe • High refractive	<ul> <li>Rapid surface oxidation</li> <li>Hard to work with and conductive</li> </ul>	• Optical coatings
SiO <sub>2</sub> • Excellent insulator • Easy to work with	• Large absorption band in the 8 - 12 $\mu$ m range	<ul><li>Electrical isolation</li><li>Surface passivation</li><li>Optical coatings</li></ul>
<ul> <li>Si<sub>3</sub>N<sub>4</sub> • Durable and heat resistant</li> <li>• Low thermal expansion</li> </ul>	<ul> <li>Large absorption band in the 10 - 14</li> <li>μm range</li> </ul>	<ul><li>Electrical isolation</li><li>Surface passivation</li><li>Optical coatings</li></ul>
<ul> <li>TiO<sub>2</sub> • High dielectric constant</li> <li>Easy to work with</li> </ul>	• Low quantum efficiency	<ul><li>Interfacial layers</li><li>Thick layers</li><li>UV Photovoltaics</li></ul>
<ul> <li>Y<sub>2</sub>O<sub>3</sub> • High breakdown strength</li> <li>Low compressive stress</li> </ul>	• Difficult to etch applications	<ul> <li>Robust, damage resistance</li> <li>LWIR transparent devices</li> <li>UV Photovoltaics</li> </ul>
<ul><li>ZnO • Long transparency</li><li>• Large bond strength</li><li>• No phase changing</li></ul>	<ul> <li>Naturally conductive</li> <li>Difficult to dope</li> <li>Fractal growth effects mechanisms</li> <li>High solubility</li> <li>Columnar microstructure</li> </ul>	<ul><li> UV transparent devices</li><li> Ohmic contacts</li></ul>
ZnSe • Long transparency • High refractive index	<ul> <li>Soft material</li> <li>Difficult to work with</li> <li>Difficulty with adherence</li> </ul>	<ul><li> LWIR transparent devices</li><li> Optical coatings</li></ul>

Table 4.1: Summary of the properties and applications of all seven materials used in this work

thermoelectric material (54), however it cannot be used at low temperatures (below 177 °C) and therefore does not work well for refrigeration (55). PbTe is a difficult material to work with using the IBSD system because it is actually a semi-metal. Its conductive nature leads to a limited amount of characterization and analysis of the electrical, optical, and structural properties. Due to the properties and difficulties, the optimized deposition parameters for PbTe were very different and did not always follow the same relationships as the dielectric materials used in this work.

There are very few reports on the preparation and deposition for PbTe, except by magnetron sputtering(56) and electron beam evaporation(57). In this work, the main utilization of PbTe was with optical coatings, used in Sections 7.3.3, 7.4.6, and 7.6.3. Table 4.2 provides some of the properties of PbTe reported by Refs. (58), (59), (60) and (61), and the following subsections will show some differences and similarities compared to the PbTe deposited in this work.

Lead Telluride (PbTe)				
Crystal system	Cubic	Density	$8.164 \text{ g-cm}^3$	
(space group)	(Fm3m)	Bandgap	$0.311 \mathrm{~eV}$	
Solubility	Insoluble	Poisson's ratio	0.26	
Transparency region	$4 - 30 \ \mu \mathrm{m}$	Young's modulus	56.9 GPa	
Elastic constants	$C_{11} = 1.0795$	Bulk modulus	39.8 GPa	
	$C_{12} = 0.0764$	Rigidity modulus	22.6 GPa	
	$C_{44} = 0.1343$	Melting point	1190 K	
Bond strength	$251 \pm 13 \text{ mol-kJ}^{-1}$	Heat capacity	$0.151 \text{ J}\text{-g}^{-1}\text{K}^{-1}$	
-		Thermal conductivity	$2.3 \text{ W-m}^{-1} \text{K}^{-1}$	

#### 4.1.1 Structural Properties

A typical deposition rate for PbTe is anywhere from 4 - 8 nm/min, and has been shown to achieve rates up to 20 nm/min with higher voltages and currents. These rates are similar to those reported by Ref. (62), but still significantly higher than all other materials used in this work. The deposition rate can be adjusted by varying any of the parameters except for substrate temperature.

Deposition of PbTe leads to very rough surfaces, with RMS values ranging from 0.44 - 5.9 nm, which is well within the range of values reported by Refs. (63) and (54). This is due to the high-energy ions altering the structural quality of the materials. PbTe has the highest penetration length of all the materials, and as a result, it is most susceptible to the spike sputtering mechanism. The unwanted effects from the spike sputtering mechanism were discussed in Section 2.3.4.

Etching of PbTe can be done quite easily. The chemical acid used for etching consists of very dilute hydrobromic based acid with portions of 200:20:1 of H<sub>2</sub>O:20 HBr:Br<sub>2</sub>. With this solution, an etch rate around 300 nm/min should be expected. Further, selective etching of pits can be used to observe the film density with a solution of 2:1 NaOH:Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>. For dry etching, CH<sub>4</sub> can be used with the same conditions as given in Table 4.3. Etch profiles similar to what is shown in Figure 4.1 should be expected.

Dry Etch Condition	ns of PbTe
Pressure	25 mTorr
Microwave Power	200 W
RF Power	300 W
CH <sub>4</sub> Flow Rate	10 sccm
$H_2$ Flow Rate	5  sccm
Substrate Temperature	30 °C
Etch Rate	$\sim 120 \text{ nm/min}$
	7

Table 4.3: Parameters used for dry etching of PbTe with an ECR system



Figure 4.1: SEM pictures of wet and dry etch profiles of PbTe

### 4.1.2 Electrical Properties

PbTe has be known to grow natively as n-type(64). The sheet resistance of the PbTe deposited had a magnitude in the  $10^3 \Omega \backslash \Box$ , for a sample with thickness of approximately 100 nm. Further, the carrier concentration values were around  $10^{19} \text{ cm}^{-3}$ , sheet carrier density around  $10^{14} \text{ cm}^{-3}$ , and mobility around 20 - 30 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>. The carrier concentration value is close to as reported by Ref. (65), but mobility values are slightly higher. While the mobility is higher, the values for the PbTe used in this work is still much lower

than reported by Ref. (66)

# 4.1.3 Optical Properties

Ellipsometry could not be used to characterize PbTe because its opaque nature restricts its transparency in the IR. However, the sample can be measured using FTIR. PbTe can be a good material for optical purposes because it has a very high refractive index. The dispersion ranges from 5.5 - 4.7, as shown in Figure 4.2. The fitted Cauchy equation can be given as:

$$n = 4.6281774 + \frac{3.739717}{\lambda^2} + \frac{-2.352101}{\lambda^2}$$
(4.1)



Figure 4.2: Dispersion of the refractive index of PbTe

In order to reduce the absorption loss in the material, nitrogen gas was used through

the secondary source. Nitrogen was chosen over argon because assistance with argon led to a higher amount of preferential sputtering on the already-deposited films. This effect does not occur or is not as significant with nitrogen because of it being a much lighter mass. While the nitrogen is useful in reducing the absorption, it also causes a reduction in the refractive index. Typically a refractive index around n = 5.5(57) is expected, but with the nitrogen assistance the lower boundary of the refractive index range was achieved.

One issue that may need to be considered is the fact that PbTe oxidizes rapidly when exposed to atmosphere. The result of this is the formation of a chemical bond in the form of Pb-O and Te-O(67). The Pb-O bond will appear in the absorption spectra, as shown in Figure 4.3. There are two absorption bands associated with this bond(57), one located around 600 cm<sup>-1</sup> and the other around 740 cm<sup>-1</sup>. In this situation, the intensity of the lower band is slightly higher. A third band is expected to be seen around 1500 cm<sup>-1</sup>, and in this case, the band is present but with a very low intensity. Finally, an absorption band is located around 2613 cm<sup>-1</sup>, characteristic to the material(68).

#### 4.1.4 Summary

Table 4.4 provides a summary of the general relationships between characterization and deposition parameters of PbTe. This information can be used to know what general parameters need to be adjusted in order to achieve specific material characteristics. The arrows represent the trend observed in the characterization results for increasing values in the deposition parameters listed on the left. A  $\downarrow$  indicates a lower characterization result,  $\uparrow$  for a higher results, and - for no change. If a  $\downarrow\uparrow$  is given, then this indicates that the



Figure 4.3: Absorption coefficient curve of PbTe

relationship will initially decrease, reach a minimum and then change to increase. This is similar for  $\uparrow\downarrow$  with an initial increase, reaching a maximum and then change to decrease. For  $\downarrow$ , this means that no change is seen initially, but towards higher parameter values the characterization value will decrease.

# 4.2 Silicon Dioxide (SiO<sub>2</sub>)

Silicon dioxide is one of the most extensively studied and known thin-film materials. It is widely used in the electronics industry for applications such as gate insulators in CMOS devices, protective layers for integrated circuits, and insulating layers for waveguide and semiconductors.  $SiO_2$  is also commonly used in very-large-scale-integration devices as an

Increasing values in:	Deposition Rate	RMS Roughness	Refractive Index	Absorption Coefficient
Beam current	-↑	$\uparrow\downarrow$	-	-↓
Beam voltage	$\uparrow$	Î	-	$\uparrow$
Dep. source Ar flow	$\downarrow$	↓-	-	$\uparrow$
Assist source $N_2$ flow	$\downarrow$	$\downarrow$	↑	$\downarrow$
Assist source power		$\downarrow\uparrow$	-	$\downarrow\uparrow$
Substrate temp	$\downarrow$	$\uparrow$	-	$\uparrow$
Substrate angle	$\downarrow\uparrow$	Ļ	-	Ļ

Table 4.4: Summary of the relationship between characterization results and deposition parameters of PbTe

insulation layer, sidewall spacer, and a protective mask due to being insoluble in water and in almost all acids, except hydrofluoric acid(55). The main reason why  $SiO_2$  is a common choice for an insulator is because it has excellent electrical properties including high dielectric breakdown field strength and low electrical defect density(69).

The preparation of SiO<sub>2</sub> can be achieved by many different techniques and have been reported in the literature by CVD(70)(71)(72)(73), thermal oxidation of silicon(74), RF magnetron sputtering(9)(75), ion-assisted evaporation(76)(77)EBE(78), IBSD(79), and electron-cyclotron resonance (ECR) microwave PECVD(80). The properties of ideal SiO<sub>2</sub> are given in Table 4.5(81), XRD angles are given in Table 4.6, and the following subsections will show some differences and similarities compared to the SiO<sub>2</sub> deposited in this work.

#### 4.2.1 Structural Properties

The deposition rate of  $SiO_2$  ranged from 1.9 - 3.2 nm/min. These values are much lower than reported by Ref. (82). The deposition rate and sputtering yield were found to be

Silicon Dioxide $(SiO_2)$			
Crystal system	Trigonal	Density	$2.63 \text{ g-cm}^3$
(space group)	$(P3_12)$	Bandgap	8.4  eV
Solubility	Insoluble	Poisson's ratio	0.08
Transparency region	$0.16$ - $4.0~\mu{\rm m}$	Young's modulus	95.0 GPa
Elastic constants	$C_{11} = 0.8680$	Bulk modulus	33.0 GPa
	$C_{12} = 0.0704$	Rigidity modulus	44.9 GPa
	$C_{13} = 0.1191$	Melting point	845.0 K
	$C_{14} = -0.1804$	Heat capacity	$0.74 \text{ J}\text{-g}^{-1}\text{K}^{-1}$
	$C_{33} = 1.0575$	Thermal conductivity	$7.5 \text{ W-m}^{-1} \text{K}^{-1}$
	$C_{44} = 0.5820$	Hardness	$741 \text{ kg-mm}^2$
Bond strength	$251 \pm 13 \text{ mol-kJ}^{-1}$		-

Table 4.5: Properties of  $SiO_2$ 

d	hkl	$2\theta$	d	hkl	$2\overline{\theta}$
4.251	100	20.85	1.9780	221	80.05
3.342	101	26.65	1.1843	114	81.15
2.457	110	36.54	1.1804	310	81.47
2.282	102	39.46	1.1532	311	83.32
2.231	111	40.29	1.1402	204	84.97
2.127	200	42.47	1.1143	303	87.46
1.9792	201	45.81	1.0813	312	90.86
1.8179	112	50.14	1.0635	400	92.82
1.8021	003	50.61	1.0476	105	94.66
1.6719	202	54.87	1.0438	401	95.12
1.6591	103	55.33	1.0347	214	96.22
1.6082	210	57.24	1.0150	223	98.74
1.5418	211	59.95	0.9898	402	102.20
1.4536	113	64.08	0.9873	313	102.56
1.4189	300	65.76	0.9783	304	103.88
1.3820	212	67.75	0.9762	320	104.20
1.3752	203	68.13	0.9636	205	106.14
1.3718	301	68.32	0.9607	321	106.61
1.2880	104	73.46	0.9284	410	112.13
1.2558	302	75.67	0.9181	322	114.08
1.2285	220	77.66	0.9161	403	114.66
1.1999	213	79.88	0.9089	224	115.89

Table 4.6: XRD angles for  $SiO_2$ 

mainly influenced by the beam current and substrate angle, and this is how different rates can be achieved.

The surface of the  $SiO_2$  films were smooth with very low RMS roughness values between 0.15 - 0.30 nm. No parameters were found to have a significant effect on the surface morphology. There may have been a change, but it was minimal because the films were very smooth already. One exception is with the substrate angle, where a dramatic change in morphology occurs when the substrate is angled either mainly towards the assist ion source or mainly towards the target. Therefore, smoother surfaces are obtained when choosing an angle that is in-between. The smooth surface can be attributed to the small grain sizes

Etching of SiO<sub>2</sub> is very simple and the conditions are well established. The dielectric can be etched using buffered HF acid. With an undiluted solution, etch rates around 1.5 - 4 nm/sec were achieved. Furthermore, dry etching can be done using a CF<sub>4</sub> based chemistry. Parameters that were used for the dry etching is given are Table 4.7. The etch rate and profile, shown in Figure 4.4, are highly dependent on the growth orientation and film density. It was found that parameters such as high substrate temperatures and substrate angles closer to the secondary source leads to lower etch rates and more vertical sidewalls. The most significant change in etch rate was observed with adjustment of the oxygen flow rate in the secondary ion source. There was a very large difference when comparing SiO<sub>2</sub> deposited with and without the secondary ion source, where the etch rates jumps to values greater than 14 nm/sec.

Dry Etch Condition	ns of $SiO_2$
Pressure	5 mTorr
Microwave Power	$200 \mathrm{W}$
RF Power	$300 \mathrm{W}$
$CF_4$ Flow Rate	20  sccm
Substrate Temperature	30 °C
Etch Rate	$\sim 85~\mathrm{nm}/\mathrm{min}$

Table 4.7: Parameters used for dry etching of  $SiO_2$  with an ECR system



Figure 4.4: SEM pictures of wet and dry etch profiles of SiO<sub>2</sub>

### 4.2.2 Electrical Properties

The sheet resistance of the SiO<sub>2</sub> deposited had a magnitude in the  $10^{12} \Omega \square$  range, for a film thickness of approximately 100 nm. Further, the carrier concentration values were around  $10^{16} \text{ cm}^{-3}$ , sheet carrier density around  $10^{11} \text{ cm}^{-3}$ , and mobility around 70 - 80 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.

The oxide capacitance was measured to be between 50 - 90 pF. This was found to vary mainly with the oxygen flow in the secondary source. Variation in the flatband voltage

can be achieved for similar reasons with values ranging from -1.5 V to 6 V. The fixed oxide charge was on the order of  $10^{11}$  cm<sup>-3</sup>, and the density of interface states ranged from 2.6 - 2.9  $10^9$  ev<sup>-1</sup> cm<sup>-2</sup>

### 4.2.3 **Optical Properties**

The refractive index of SiO<sub>2</sub> is expected to be around 1.47 - 1.46(9)(83)(84), which is similar to the experimentally obtained values (n = 1.6 - 1.3). This range was mainly influenced by the secondary ion-source parameters, ion-beam current, and substrate temperatures. The dispersion of the refractive index was fitted to the Cauchy equation, shown in Figure 4.5, given as:

$$n = 1.41870 + \frac{0.12886725}{\lambda^2} + \frac{2.7573641 \times 10^{-5}}{\lambda^4}$$
(4.2)

In addition to the introduction of  $O_2$  being necessary for achieving the appropriate refractive index, it is also necessary for good transparency(79). The presence of absorption bands in the far-infrared wavelength range makes this material a poor choice for optical applications in the far-infrared. There are three absorption bands that are expected to appear(58). The first one is located at 1087 cm<sup>-1</sup> and has a FWHM of 128.5 cm<sup>-1</sup>, as shown in Figure 4.6. This band is due to Si-O stretching vibrations and is important because any shift of the band to longer wavelengths or change in intensity is a good indication of either a higher oxygen content, higher amount of bond strain, or lower film density(17)(83). In general if the shift is due to a lower film density, the change in density



Figure 4.5: Dispersion of the refractive index of  $SiO_2$ 

can be found proportional to the shift in wavenumber(76). If the change is due to a higher oxygen content, then the absorption band should exhibit a decrease in intensity without any shift in position(79). Further, there is an indication of the formation of a native oxide layer between the substrate and dielectric due to the presence of a shoulder(83) on the band around 1250 cm<sup>-1</sup>. A second absorption band is located at 837 cm<sup>-1</sup> because of bond rocking(85), and a third absorption band is located at 461 cm<sup>-1</sup> due to bond bending. The intensity of the bond rocking band can be a relative indication of point defects present in the material(85). If both the bond rocking and stretching vibrations band shift to a higher frequency, this is an indication of higher bond angles between Si and O atoms(76). Finally, there are extra two absorption bands that have been reported in the spectra of others(9)(76). One absorption band is located around 950 cm<sup>-1</sup> bonds, and the other is located around  $3600 \text{ cm}^{-1}$ . When a sample is exposed to air after the deposition, the sample can react with hydrogen atoms in the air and form either Si-OH bonds or O-H bonds from the adsorbed water. One way to avoid this or alleviate the problem is by adjusting the argon gas flow through the deposition source or by using a capping layer. The absence of both bands in Figure 4.6 indicates that the sample does not contain pores filled with water. An experimental verification of this is provided in Section 2.4.



Figure 4.6: Absorption coefficient curves of SiO<sub>2</sub>

## 4.2.4 Summary

Table 4.8 provides a summary of the general relationships between characterization and deposition parameters of  $SiO_2$ . This information can be used to know what general

parameters need to be adjusted in order to achieve specific material characteristics. A description of the notation is given in 4.1.4.

Increasing	Deposition	RMS	Film	Refractive	Absorption
values in:	Rate	Roughness	Density	Index	Coefficient
Beam current	$\uparrow$	1	$\uparrow\downarrow$	$\downarrow$	$\downarrow$
Beam voltage	↑	$\uparrow\downarrow$	↑	↑	
Dep. source Ar flow	↑	$\downarrow$		↑	↑
Assist source $O_2$ flow	$\downarrow$	$\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\uparrow\downarrow$
Assist source power	$\uparrow\downarrow$	$\downarrow$	$\downarrow\uparrow$	↑-	$\downarrow\uparrow$
Substrate temp	↓-	$\uparrow\downarrow$	$\uparrow\downarrow$	-↓	$\uparrow\downarrow$
Substrate angle	$\uparrow$	$\downarrow\uparrow$	$\downarrow$	-	↓-

Table 4.8: Summary of the relationship between characterization results and deposition parameters of  $SiO_2$ 

# 4.3 Silicon Nitride $(Si_3N_4)$

Silicon nitride is another common insulating material, alongside with SiO<sub>2</sub>, used in many electronic devices. Si<sub>3</sub>N<sub>4</sub> is used for optoelectronics, photonic devices, LEDs, microelectronics(59), and memory circuits(86). Its chemical and electrical durability makes it a hard, lightweight, heat resistant ceramic, important for applications that must endure harsh environmental conditions. Si<sub>3</sub>N<sub>4</sub> is an excellent material for protection against ions, contaminants, and moisture. In addition, it has a low thermal expansion, good resistance to corrosion and thermal shock, and high dielectric constant.

The properties of ideal  $Si_3N_4$  is provided in Table 4.9(58)(59)(87)(88) with XRD angles given in Table 4.10. This dielectric is typically prepared using CVD methods, and information can be found in Ref. (87) and (89). The following subsections will show some

Silicon Nitride $(Si_3N_4)$			
Crystal system	Hexagonal	Density	$3.24 \text{ g-cm}^3$
(space group)	$(P6_{3}/m)$	Bandgap	5.0  eV
Solubility	Insoluble	Poisson's ratio	0.24
Transparency region	$0.30$ - $4.6~\mu{\rm m}$	Young's modulus	195.05 GPa
		Melting point	2300.0 K
		Heat capacity	$0.74 \text{ J}\text{-g}^{-1}\text{K}^{-1}$
		Thermal conductivity	$33.0 \text{ W-m}^{-1} \text{K}^{-1}$

differences and similarities compared to the  $Si_3N_4$  deposited in this work.

Table 4.9: Properties of  $Si_3N_4$ 

### 4.3.1 Structural Properties

The deposition of  $Si_3N_4$  films occurred at rates around 3.2 - 4 nm/min. All system parameters demonstrated a change in the deposition rate, except the substrate angle and argon flow rate. Higher rates can be achieved with either higher RF powers, lower  $N_2$ flow rates in the secondary source, higher beam currents, higher beam voltages, and lower substrate temperatures.

In comparison to all the other materials used in this work,  $Si_3N_4$  films were the smoothest with roughness values as low as 0.112 nm and as high as 0.339 nm. Large changes in the roughness can be achieved by working with the N<sub>2</sub> flow rate.

The etching of  $Si_3N_4$  can be done by using either HF or  $H_3PO_4$  acid for wet etch and  $SF_6$  based dry etch. The wet etch rates can vary significantly, especially with HF where a very slow, but controlled etch rate of 30 - 40 nm/min can be expected. The dry etching parameters used with an ECR system is given Table 4.11. Using either technique, the

d	hkl	$2\theta$	d	hkl	$2\theta$
6.5830	100	13.44	1.1618	222	83.06
3.8000	110	23.39	1.1551	421	83.65
3.2930	200	27.06	1.1445	312	84.60
2.6600	101	33.67	1.1377	511	85.23
2.4890	210	36.05	1.0957	430	89.34
2.3100	111	38.95	1.0828	520	90.70
2.1939	300	41.11	1.0545	322	93.85
2.1797	201	41.39	1.0476	601	94.66
1.9013	220	47.80	1.0269	412	97.20
1.8916	211	48.06	1.0219	431	98.78
1.8275	310	49.86	1.0043	610	100.17
1.7525	301	52.15	0.9914	521	101.97
1.5911	221	57.91	0.9761	502	104.21
1.5467	311	59.74	0.9589	103	106.90
1.5108	320	61.31	0.9554	332	107.46
1.4534	002	64.01	0.9408	530	109.93
1.4368	410	64.84	0.9298	203	111.89
1.4325	401	65.06	0.9175	512	114.19
1.4197	102	65.72	0.9132	620	115.02
1.3579	112	69.12	0.9034	441	117.00
1.3408	321	70.13	0.8950	331	118.78
1.3299	202	70.79	0.8866	303	120.65
1.3173	500	71.57	0.8722	710	124.06
1.2883	411	73.44	0.8712	621	124.29
1.2675	330	74.85	0.8652	432	125.05
1.2554	212	75.70	0.8634	223	126.29
1.2447	420	76.47	0.8561	313	128.27
1.1998	501	79.89	0.8537	522	128.93
1.1831	331	81.25			

Table 4.10: XRD angles for  $Si_3N_4$ 



Figure 4.7: SEM pictures of wet and dry etch of  $Si_3N_4$ 

profiles are shown in Figure 4.7.

Dry Etch Condition	ns of $Si_3N_4$
Pressure	100 mTorr
Microwave Power	$200 \mathrm{W}$
RF Power	$300 \mathrm{W}$
He Flow Rate	20  sccm
SF <sub>6</sub> Flow Rate	15  sccm
Substrate Temperature	$30 \ ^{\circ}\mathrm{C}$
Etch Rate	$\sim 60 \text{ nm/min}$
	,

Table 4.11: Parameters used for dry etching of  $\mathrm{Si}_3\mathrm{N}_4$  with an ECR system

## 4.3.2 Electrical Properties

Sheet resistance values in the range of  $10^{13} \Omega \backslash \Box$  for a 100 nm thick film were measured using the Hall system. Further, the carrier concentration values were around  $10^{12} \text{ cm}^{-3}$ , sheet carrier density around  $10^{15} \text{ cm}^{-3}$ , and mobility around 72 - 85 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.

A capacitance between 40 - 50 pF was measured with the  $\rm Si_3N_4$  MIS structures. This

value is slightly higher than achieved in Ref. (90). The flatband voltage was found to be 2.25 V from ideal with indication of negative fixed oxide charges present in the films. The density of the fixed oxide charges were found to be  $Q_f = 1.11 \times 10^{-12} \text{ cm}^{-3}$ . The charge of the dielectric can be changed mainly by adjusting the N<sub>2</sub> flow in the secondary source. Higher flow rates demonstrated a shift in the curve towards positive flatband voltages and therefore leading to a more negatively charged material. This is different from the positively charge material achieved by PECVD, and the polarity difference is speculated to be because of the formation of N-H bonds(91). Finally, the density of interface states was found to be  $D_{it} = 5.9 \times 10^9 \text{ eV}^{-1} \text{ cm}^{-2}$ .

### 4.3.3 Optical Properties

The refractive index of  $Si_3N_4$  deposited in this work ranged from 2.1 - 2.0. These values are similar to values reported in Ref. (90) and (58). There was not a significant variation in the refractive index because the deposition parameters showed no significant effects. The only exception was with the N<sub>2</sub> flow through the secondary source. The dispersion of refractive index in the material is shown in Figure 4.8 and can be represented by the Cauchy equation as:

$$n = 2.0019336 + \frac{0.15265213}{\lambda^2} + \frac{4.0495557}{\lambda^4}$$
(4.3)

The  $N_2$  gas can be used in the assistance source to compensate for any loss due to preferential sputtering. Without assistance, the films were found to be Si rich, similar to Ref. (92).



Figure 4.8: Dispersion of the refractive index of  $Si_3N_4$ 

Similar to SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub> is a poor choice for optical applications in the far infrared. Characteristic to the material, absorption bands were observed in Figure 4.9 at 930 cm<sup>-1</sup> and 493 cm<sup>-1</sup> due to Si-N stretching vibrations(93). The presence of two bands is due to one band being an overtone of the other. The materials showed no reaction to air after the deposition. Reaction of the sample with air would lead to chemical reactions between Si-H and N-H. This can be confirmed by the presence of bands around 3340 cm<sup>-1</sup>, 2000 cm<sup>-1</sup>, and 1175 cm<sup>-1</sup> due to stretching and bending vibrations. Any changes in the location and shape of the bands are due to many different things. One is due to composition change which causes a shift in any of the bands, except the N-H band. In general, if it shifts to a lower number then the material is Si-rich, and shifts to a higher number indicate a more N-rich material. A second one is as a result of higher compressive stress or more dense films(94), determined by higher intensities of the bands due to Si-N. The dielectric constant of the material was found to be  $\varepsilon = 3.6$ , which is much lower than



Figure 4.9: Absorption coefficient curve of  $Si_3N_4$ 

reported in Ref. (90).

# 4.3.4 Summary

Table 4.12 provides a summary of the general relationships between characterization and deposition parameters of  $Si_3N_4$ . This information can be used to know what general parameters need to be adjusted in order to achieve specific material characteristics. A description of the notation is given in 4.1.4.
Increasing values in:	Deposition Rate	RMS Roughness	Refractive Index	Absorption Coefficient
Beam current	<u></u>	-	_	1
Beam voltage	$\uparrow$	$\uparrow$	-	$\uparrow$
Dep. source Ar flow	$\downarrow\uparrow$	-	-	-↑
Assist source $N_2$ flow	$\downarrow$	↑	$\downarrow$	-↑
Assist source power	↑	$\downarrow\uparrow$	-	↑
Substrate temp	$\downarrow$	-	-	
Substrate angle	$\uparrow$	$\downarrow\uparrow$	Ť	$\downarrow\uparrow$

Table 4.12: Summary of the relationship between characterization results and deposition parameters of  $Si_3N_4$ 

## 4.4 Titanium Dioxide (TiO<sub>2</sub>)

Titanium dioxide is one of the most well studied thin-film materials due to accessibility and simplicity. It is used for many applications such as optoelectronics, gas sensing, optical coatings, very large scale integrated (VLSI) circuits(95), and microelectronics such as capacitors and sensors. Another application is pigmentation for paints and colors where  $TiO_2$  is a good choice because of its transparency in the visible and near IR. It has good insulating properties such as a high dielectric constant. Further,  $TiO_2$  is a strong material with excellent mechanical and chemical stability in adverse environmental conditions.

The preparation of  $\text{TiO}_2$  has been done by EBE(96)(97), IBSD(98), ion-assisted deposition(99), dip coating(100), and thermal oxidation of metal(101). The properties reported in the literature are provided in Table 4.13(81), XRD angles in Table 4.14(102), and the following subsections will show some differences and similarities compared to the TiO<sub>2</sub> deposited in this work.

	Titanium Dioxide ( $11O_2$ )						
Crystal system	Tetragonal	Density	$4.26 \text{ g-cm}^3$				
(space group)	$(P4_2/mm)$	Bandgap	3.5  eV				
Solubility	0.001g:100g H <sub>2</sub> O	Poisson's ratio	0.27				
Transparency region	0.42 - 4.0 μm	Young's modulus	293.0 GPa				
Elastic constants	$C_{11} = 2.7143$	Bulk modulus	215.0 GPa				
	$C_{12} = 1.7796$	Rigidity modulus	115.0 GPa				
	$C_{13} = 1.4957$	Melting point	845.0 K				
	$C_{14} = -0.1804$	Heat capacity	$0.69 \text{ J}\text{-g}^{-1}\text{K}^{-1}$				
	$C_{33} = 4.8395$	Thermal conductivity	$7.4 \text{ W-m}^{-1} \text{K}^{-1}$				
	$C_{44} = 1.2443$	Hardness	$879 \text{ kg-mm}^2$				
Bond strength	$672.4 \pm 9.2 \text{ mol-kJ}^{-1}$		<u> </u>				

Table 4.13: Properties of  $TiO_2$ 

d	hkl	$2\theta$	d	hkl	$2\theta$
3.5150	101	25.32	1.0436	321	95.14
2.4310	103	36.95	1.0182	109	98.32
2.3780	004	37.80	1.0070	208	99.80
2.3320	112	38.57	0.9967	323	101.22
1.8920	200	48.05	0.9555	316	107.45
1.6999	105	53.89	0.9464	400	108.96
1.6665	211	55.06	0.9246	307	112.84
1.4930	213	62.12	0.9192	325	113.85
1.4808	204	62.69	0.9138	411	114.91
1.3641	116	68.76	0.8966	219	118.44
1.3378	220	70.31	0.8890	228	120.11
1.2795	107	74.03	0.8819	413	121.73
1.2649	215	75.03	0.8793	404	122.34
1.2509	301	76.02	0.8464	420	131.02
1.1894	008	80.72	0.8308	327	135.98
1.1725	303	82.14	0.8268	415	137.38
1.1664	224	82.66	0.8102	309	143.86
1.1608	312	83.15	0.7974	424	150.04
1.0600	217	93.22	0.7928	0012	152.62
1.0517	305	94.18			

Table 4.14: XRD angles for  $TiO_2$ 

The deposition of  $\text{TiO}_2$  was done in this work using two different types of sputtering: compound and reactive. Each one has its advantages and disadvantages, as discussed in Section 6.2.1. The properties of the films were similar in some respects, while still having differences as shown in this section. The appropriate choice should be made dependent on the objective.

#### 4.4.1 Structural Properties

The deposition rate for  $\text{TiO}_2$  can range from 2- 4 nm/min with variation achieved mainly by varying the oxygen flow rate through the secondary source. These rates are similar to reported values given in Ref. (15). Transitioning from no oxygen assistance to a slight incorporation of oxygen was shown to abruptly lower the rate(103).

The morphologies of the samples were different for compound sputtering and reactive sputtering. The surface was smooth for compound sputtering, with RMS values ranging from 0.2 - 0.5 nm. This is different from reactive sputtering which has very rough surfaces with roughness values around 2.5 - 7.0 nm(104). With an average grain size of  $15 \text{ nm}^2(105)$ , the rough surfaces cannot be due to the large sizes. Instead the roughness is due to random hill like features due to nucleation. The surface can be smoothed out by adjusting the gas flow rates, beam current, and substrate temperature. For example, higher argon gas flow rates leads to large grain sizes and a rougher surface(106).

The etching of  $TiO_2$  is similar to  $SiO_2$  where HF acid can be used as a chemical acid etch and  $CF_4$  chemistry for dry etching. However, the etch rate is faster, especially with HF, with rates around 22 nm/sec. Further, the dry etching parameters used with an ECR

Dry Etch Condition	ns of $TiO_2$
Pressure	1 mTorr
Microwave Power	$200 \mathrm{W}$
RF Power	$200 \mathrm{W}$
$CF_4$ Flow Rate	30  sccm
Substrate Temperature	$30 \ ^{\circ}\mathrm{C}$
Etch Rate	$\sim 65 \ \mathrm{nm}/\mathrm{min}$
$CF_4$ Flow Rate Substrate Temperature Etch Rate	$\begin{array}{l} 30 \text{ sccm} \\ 30 \text{ °C} \\ \sim 65 \text{ nm/min} \end{array}$

system is given Table 4.15. Using either technique, the profiles are shown in Figure 4.10.

Table 4.15: Parameters used for dry etching of  ${\rm TiO}_2$  with an ECR system



Figure 4.10: SEM pictures of wet and dry etch profiles of  $TiO_2$ 

### 4.4.2 Electrical Properties

The sheet resistance of the TiO<sub>2</sub> deposited had a magnitude in the  $10^{11} \Omega \square$  range, for a thickness around 100 nm. Further, the carrier concentration values were around  $10^{15}$ cm<sup>-3</sup>, sheet carrier density around  $10^{10}$  cm<sup>-3</sup>, and mobility around 0.1 - 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>

#### 4.4.3 **Optical Properties**

The refractive indices that were experimentally achieved with TiO<sub>2</sub> ranged from 2.2 - 2.1. Similar values were reported by Ref. (107), but higher values were reported by Ref. (9). The low refractive index and deposition conditions are most likely an indication of the material having a rutile phase. There was only one exceptional case where the refractive index had a very high value of 2.9. This occurred when the RF power in the secondary source was very low. Similar to  $Si_3N_4$ , the deposition parameters had barely any effects on changing the refractive index. The only exceptions are the flow rates and power of the assistance source and the flow rate of the argon bombarding the target(10). The Cauchy equation was fitted to the data points in Figure 4.11, following the relationship:

$$n = 2.2177966 + \frac{1.4427049}{\lambda^2} + \frac{-3.3626663}{\lambda^2}$$
(4.4)

Oxygen gas was used to improve the stoichiometry of the films and achieve a refractive index that is close to bulk. The  $O_2$  incorporation works extremely well with reactive sputtering because the atoms can then react easier with a low heat of formation(9).

The transparency of TiO<sub>2</sub> is around 8  $\mu$ m and observed in the absorption spectra, given in Figure 4.12. There are two bands that uniquely identify TiO<sub>2</sub>. The first band is due to Ti-O stretching vibrations(108). It showed a very high peak intensity of  $\alpha = 1888$  cm<sup>-1</sup> located at 526 cm<sup>-1</sup>. A shoulder on this band can be seen at 634 cm<sup>-1</sup>. Finally, one additional band appeared due to reaction with exposed air. These bands have formed at 2260 cm<sup>-1</sup> because of stretching vibrations between the O-H bond.



Figure 4.11: Dispersion of the refractive index of  $TiO_2$ 

Finally the last optical property is the bandgap. In this work, the bandgap was measured using ellipsometry and Tauc's law, having a value of 3.16 eV.

### 4.4.4 Summary

Table 4.16 provides a summary of the general relationships between characterization and deposition parameters of  $TiO_2$ . This information can be used to know what general parameters need to be adjusted in order to achieve specific material characteristics. A description of the notation is given in 4.1.4.



Figure 4.12: Absorption coefficient curve of  $TiO_2$ 

# 4.5 Yttrium Oxide $(Y_2O_3)$

Yttrium oxide has recently become an attractive alternative insulator to  $SiO_2$  due to its high dielectric constant, high breakdown strength, and low lattice mismatch with substrates like silicon. This material is also desirable because of its low leakage currents(109)(110) which can become a performance limiting factor. It has many other unique properties like having one the highest affinities to oxygen, resistance to tunneling(111), and high temperature stability up to 2325 °C(112). The Y<sub>2</sub>O<sub>3</sub> insulator has been used in applications such as large-scale integration (LSI) capacitors(113), memory cells(114), and CMOS transistors(115). Its high thermal conductivity and crystallographic stability makes it commonly used in waveguides(116).

Increasing	Deposition	RMS	Refractive	Absorption
values in:	Rate	Roughness	Index	Coefficient
Beam current	1	$\uparrow \downarrow$	-	-
Beam voltage	↑	$\downarrow$	-	$\downarrow$
Assist source $O_2$ flow	↑	$\downarrow\uparrow$	↓-	↓-
Assist source power	$\downarrow\uparrow$	$\downarrow$	↓-	^-
Substrate temp	$\uparrow \downarrow$	$\downarrow\uparrow$	^-	$\uparrow$

Table 4.16: Summary of the relationship between characterization results and deposition parameters of  $TiO_2$ 

The preparation of  $Y_2O_3$  can be achieved by many different techniques: EBE(97)(117), IBSD(2)(118), CVD(119), and PLD(120). The properties of bulk  $Y_2O_3$  can be found in Table 4.17 (81)(121).

Yttrium Oxide $(Y_2O_3)$						
Crystal system	Cubic	Density	$5.01 \text{ g-cm}^3$			
(space group)	(Ia3)	Bandgap	5.6  eV			
Solubility	$1 \times 10^{-5} g: 100 g H_2 O$	Poisson's ratio	0.30			
Transparency region	0.29 - 7.1 μm	Young's modulus	173.0 GPa			
Elastic constants	$C_{11} = 2.3300$	Bulk modulus	145.0 GPa			
	$C_{12} = 1.0100$	Rigidity modulus	67.0 GPa			
	$C_{44} = 0.6700$	Melting point	2650.0 K			
Bond strength	$719.6 \pm 11.3 \text{ mol-kJ}^{-1}$	Heat capacity	$0.4567 \text{ J}\text{-g}^{-1}\text{K}^{-1}$			
		Thermal conductivity	$13.5 \text{ W-m}^{-1} \text{K}^{-1}$			

Table 4.17: Properties of  $Y_2O_3$ 

## 4.5.1 Structural Properties

Typical deposition rates for  $Y_2O_3$  range from 2 - 2.8 nm/min, which is on the lower end of values reported by Ref. (2). This range is not as wide as ones for the other materials,

d	hkl	$2\theta$	d	hkl	$2\theta$
3.8050	101	23.36	1.2965	420	72.90
3.7700	020	23.58	1.2920	332	73.20
3.3960	111	26.22	1.2769	341	74.21
2.6760	121	33.46	1.2751	104	74.33
2.5930	210	34.56	1.2713	152	74.59
2.4430	201	36.76	1.2574	114	75.56
2.3678	102	37.97	1.2499	313	76.09
2.2592	112	39.87	1.2481	143	76.22
2.2276	220	40.46	1.2382	024	76.94
2.0497	221	45.15	1.2219	402	78.16
1.8831	040	48.29	1.2101	430	79.07
1.8582	230	48.98	1.2062	412	79.38
1.8434	212	49.40	1.2015	323	79.75
1.7376	301	52.63	1.1923	161	80.49
1.7230	132	53.11	1.1841	204	81.16
1.6878	141	54.31	1.1810	252	81.42
1.6665	103	55.06	1.1699	214	82.36
1.5772	321	58.47	1.1623	422, 243	83.02
1.5291	042	60.50	1.1384	351	85.16
1.5157	123	60.73	1.1176	153	87.14
1.5066	232	61.09	1.1137	440	87.52
1.4764	302	61.50	1.0987	432	89.03
1.4482	203	62.90	1.0894	441	90.00
1.4286	033	64.96	1.0833	403	90.64
1.3883	133	67.40	1.0809	501	90.90
1.3752	223	68.13	1.0758	044	91.45
1.3583	410	69.10	1.0708	234	92.00
1.3229	250	71.22	1.0699	511	92.10
1.3107	004	71.99			

Table 4.18: XRD angles for  $Y_2O_3$ 

however the largest change can be achieved by adjustment of the assist source RF power.

The surface of the films were very smooth with roughness values ranging from 0.11 - 1.7 nm. AFM also showed an average grain size to be around 83 nm<sup>2</sup>, similar to values reported in Ref. (122). Smooth surfaces were achieved using low RF powers in the secondary source and intentional heating of the substrate.

Etching of  $Y_2O_3$  is one the biggest challenges with the material. It is very difficult to etch due because it has a large affinity to oxygen and a very strong bond strength between the Y-O atoms. While this makes  $Y_2O_3$  a chemically stable material (117), this also makes etching the most difficult of all the seven materials. It is resistant to almost all acids, including HF, and has a low solubility to water. One acid that was reported to etch YCuBaO(123)(124) was  $H_3PO_4$  and  $HNO_3$ , so this was attempted. Using a mixture of  $1:10 \text{ H}_3\text{PO}_4:\text{H}_2\text{O}$ , the material was etched with a rate that varies between 18 - 21 nm/min. The sidewalls may not be as vertical as desired, but variations in the ratios can be made to achieve this. One precaution that must be considered is that this acid mixture will attack the photoresist. Typically used photoresists, AZ 5214 and AZ 4330, were found to be attacked by the phosphoric acid. A 3-4  $\mu$ m thickness of photoresist is sufficient to withstand the attack for approximately 20 sec. Beyond this, the acid will begin to etch the photoresist first before it etched the material. This is especially the case at the photoresist/ $Y_2O_3$  interface. Eventually the acid will etch the layer at the interface, removing any adhesion to the dielectric and causing the photoresist to peel off. Dry etching of material needs to be mainly through physical bombardment using Ar, and  $Cl_2$  can be used to form Y-Cl bonds and help etch the material. The conditions are given

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in Table 4.19, and SEM pictures of the etch profile are shown in Figure 4.13.

When  $Y_2O_3$  is dry etched, the most effective gases to use are  $Cl_2$  and Ar(125). The highly energetic argon atoms are needed to break the Y-O bonds, which is the dominant etch mechanism. The  $Cl_2$  gas is then used to form Y-Cl(126) and enhance the etching process. Higher etch rates can be achieved by using a higher  $Ar/(Ar+Cl_2)$  ratio. However, the etch process is still very slow. The rate may need to be reduced because if the argon flow is too high, issues such as surface damage and curing of the photoresist can arise. Prevention of the photoresist from curing was done by find an optimal value with minimal bombardment while having high enough etch rates to prevent surface overheating. This lead to a tradeoff between etching with lower RF powers and a lower  $Ar/(Cl_2 + Ar)$  ratio which would lead to lower amount of Ar bombardment but significantly lower etch rates.

Dry Etch Condition	ns of $Y_2O_3$
Pressure	2 mTorr
Microwave Power	$200 \mathrm{W}$
RF Power	$300 \mathrm{W}$
$Cl_2$ Flow Rate	5  sccm
Ar Flow Rate	20  sccm
Substrate Temperature	30 °C
Etch Rate	$\sim 13~\mathrm{nm}/\mathrm{min}$

Table 4.19: Parameters used for dry etching of  $Y_2O_3$  with an ECR system

X-ray peaks can be found at angles provided in Table 4.18(127)(123). Changes in the crystallinity of  $Y_2O_3$  can be made in many ways. One way to make the materials more crystalline is to enhance the thin underlying oxide layer that has formed on the substrate, since the Y metal atom will nucleate with native oxide layers such as SiO<sub>2</sub>(128). The



Figure 4.13: SEM pictures of wet and dry etch profiles of  $Y_2O_3$ 

crystalline state of  $Y_2O_3$  is also highly dependent on both the substrate temperature and oxygen partial pressure. This was demonstrated by Ref. (115) showing a change in temperature from 150 °C to 350 °C or the reduction of  $O_2$  gas pressure led to the transformation from amorphous to polycrystalline.

## 4.5.2 Electrical Properties

The sheet resistance of the  $Y_2O_3$  deposited had a magnitude in the  $10^{11} \Omega \square$  range, for a thickness of 100 nm. Further, the carrier concentration values were around  $10^{13} \text{ cm}^{-3}$ , sheet carrier density around  $10^8 \text{ cm}^{-3}$ , and mobility around  $1000 - 2000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ 

## 4.5.3 Optical Properties

The Cauchy equation, shown in Figure 4.14, was fitted to the data points for the refractive index of  $Y_2O_3$  given as:

$$n = 1.7297 + \frac{0.027076449}{\lambda^2} + \frac{-0.0010292134}{\lambda^4}$$
(4.5)

This is similar to values reported in Ref. (129). The value obtained can be adjusted by using different parameters, such as higher substrate temperatures in order to achieve a higher refractive index.



Figure 4.14: Dispersion of the refractive index of  $Y_2O_3$ 

The absorption spectrum from a  $Y_2O_3$  deposition is shown in Figure 4.15. A total of

three absorption bands are present. The first two located around 1470 cm<sup>-1</sup> and 4468 cm<sup>-1</sup> are due to O-H-O stretching(130). The third band is located between 715 - 1000 cm<sup>-1</sup>. This is due to lattice absorption which causes the gradual increase observed(131). The presence of another band that has been reported(122) is around 557 cm<sup>-1</sup>.



Figure 4.15: Absorption coefficient curve of  $Y_2O_3$ 

### 4.5.4 Summary

Table 4.20 provides a summary of the general relationships between characterization and deposition parameters of  $Y_2O_3$ . This information can be used to know what general parameters need to be adjusted in order to achieve specific material characteristics. A description of the notation is given in 4.1.4.

Increasing	Deposition	RMS	Sheet	Refractive	Absorption
values in:	Rate	Roughness	Resistance	Index	Coefficient
Beam current	1	-↑	1	^-	$\downarrow\uparrow$
Beam voltage	$\uparrow$	↑	↑	-	↓-
Dep. source Ar flow	-	↓-	↓-	-	$\downarrow$
Assist source $O_2$ flow	↑	$\downarrow\uparrow$	↓-	^-	
Assist source $O_2$ flow	$\downarrow$	^-	$\uparrow \downarrow$	-	↓-
Assist source power	1-	^-	$\downarrow$	-	^-
Substrate temp	1-	↓-	↑-	-	$\downarrow\uparrow$
Substrate angle	$\uparrow$	$\downarrow\uparrow$	-	-	$\downarrow$

Table 4.20: Summary of the relationship between characterization results and deposition parameters of  $Y_2O_3$ 

# 4.6 Zinc Oxide (ZnO)

Zinc oxide is a wide bandgap material that can be used for a diverse range of applications with effectiveness in both the visible and UV. It is used for UV LEDs, laser diodes, photodetectors, transducers, piezoelectric devices, gas sensing systems, microactuators, wireless communication systems(132), microelectronics, solar cells(133), and high power electronic devices. In addition, ZnO is found in products used by the every day user for applications such as white color pigmentation for paints and rubbers. Its absorption of UV light is also useful for cosmetic creams and sunblock. There are many desirable properties that ZnO possess. It is a direct bandgap material with large bond strength and large exciton binding energy. It also has a large piezoelectric coupling constant, which is required in surface and bulk acoustic wave devices(134). In addition, ZnO is good for elevated temperature operation because it does not have any phase changing effects like most other materials(135).

The deposition and characterization of ZnO was reported using either EBE(135)(136), CVD(137)(138), RF sputtering(139)(140), magnetron sputtering(141)(142), PLD(143), sol-gel method(144), and spray pyrolysis. The properties of ZnO are provided in Table 4.21(145)(146)(147) and XRD angles are provided in Table 4.22.

Zinc Oxide (ZnO)						
Crystal system	Hexagonal	Density	$5.6 \text{ g-cm}^3$			
(space group)	$(6 \mathrm{mm})$	Bandgap	3.35  eV			
Solubility	$1.6 \text{x} 10^{-4} \text{g} : 100 \text{g} \text{H}_2 \text{O}$	Poisson's ratio	0.35			
Elastic constants	$C_{11} = 2.0970$	Young's modulus	127.0 GPa			
	$C_{12} = 1.2110$	Bulk modulus	144.0 GPa			
	$C_{13} = 1.0510$	Rigidity modulus	47.0 GPa			
	$C_{33} = 2.1090$	Melting point	2248.0 K			
	$C_{44} = 0.4247$	Heat capacity	$0.4567 \text{ J}\text{-g}^{-1}\text{K}^{-1}$			
Bond strength	$159 \pm 4 \text{ mol-kJ}^{-1}$	Thermal conductivity	$30.0 \text{ W-m}^{-1}\text{K}^{-1}$			

Table 4.21: Properties of ZnO

#### 4.6.1 Structural Properties

The deposition of ZnO can be done using the IBSD system and rates between 1.5 - 3.0 nm/min should be expected(139)(148). The variation occurs when changes with the ion beam current, ion beam voltage, and secondary source parameters are made. ZnO exhibits a rougher surface due to its microstructure(149), shown in the left-hand picture of Figure 4.17. The rough surface is because of being more susceptible to the formation of Zone II type. The high binding energy prevents complete removal of weakly bound atoms, leading to a rougher surface than the other oxides. The samples exhibited its lowest RMS roughness of 0.7 nm and highest of 2.0 nm.

d	hkl	$2\theta$	d	hkl	$2\theta$
4.630	003	19.14	1.2166	0111	78.57
4.191	101	21.18	1.2020	128, 312	79.71
3.171	012	23.92	1.1766	0210	81.79
2.540	110	35.31	1.1512	134	84.00
2.355	015	38.18	1.1139	226	87.50
2.321	006	38.76	1.0862	042	90.33
2.228	113	40.45	1.0674	2110	92.38
2.173	021	41.52	1.0558	1112	93.71
2.097	202	43.10	1.0485	404	94.56
1.866	024	48.94	1.0069	1211	99.82
1.813	107	50.29	0.9990	318	100.90
1.619	018	56.83	0.9816	229	103.39
1.500	214	61.80	0.9702	0114	105.12
1.466	300	63.41	0.9692	324	105.27
1.428	125	65.31	0.9599	410	106.74
1.3650	208	68.71	0.9296	048	111.92
1.3276	1010	70.93	0.9175	1310	114.19
1.3218	119	71.29	0.9064	2014	116.37
1.2396	306	76.84	0.8868	416	120.58

Table 4.22:	XRD	angles	for	ZnO
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Figure 4.16: SEM pictures of wet and dry etch profiles of ZnO



Figure 4.17: SEM and illustration of the fractal growth mechanism in ZnO

ZnO is a material unique in many ways, one is with its fractal growth mechanism(150). The fractal nature of the films can be revealed by using a chemical acid etch such HNO<sub>3</sub>, CH<sub>3</sub>COOH, HCl, H<sub>2</sub>SO<sub>4</sub>, or HF. Etching of the films will reveal a pattern that consists of various pits located at the defect sites(151), and reveals the fractal characteristics of the growth. An SEM image of ZnO etched using acetic acid is shown in Figure 4.16. The formation of the pits occurs because of a few reasons and the etch pits pattern and density

indicate a number of different things. There are four patterns detected in ZnO, as shown in the right-hand picture of Figure 4.17. The pattern observed with the ZnO of this work was the pattern shown in the bottom left. The formation occurs due to the difference in etch rate between the zinc face and the oxygen face, and, in general, the fractal nature is due to the low adatom mobilities during the growth. First, a more porous film will have a higher defect density and shorter overall etch time. Detection of the formation of Zn-H bonds can be done by using HCl acid to reveal the reactions(152). Further, all the acids can be used for characterization of film density and properties by analyzing the etch pit density. The etch pits for a deposited ZnO sample etched in acid had a density of around  $1.29 \times 10^9 \text{ cm}^{-2}$ .

The defect density can be modified by changing the sputtering pressure, substrate temperature and deposition rate. Although this limits the etching of ZnO, one of the advantages is the small amount of undercut that occurs due to a higher etch rate in the vertical direction than the horizontal(152). The dry etching chemistry for ZnO includes  $CH_4$ , as given in Table 4.23. It can be noted that other chemistries can be used, such as  $Cl_2$  and  $H_2$ , but  $CH_4$  showed the most vertical sidewalls with smooth surfaces. Etching in  $Cl_2$  environment has been reported to cause surface damage(153). Additionally,  $H_2$  can be used for reducing the selectivity of the etching(154).

#### 4.6.2 Electrical Properties

The sheet resistance of the ZnO deposited had a magnitude in the  $10^5 \Omega \square$  range, for a thickness of 100 nm. Further, the carrier concentration values were around  $10^{16} \text{ cm}^{-3}$ ,

Dry Etch Conditions of ZnO					
5 mTorr					
$350 \mathrm{W}$					
$400 \mathrm{W}$					
1 sccm					
5  sccm					
30 °C					
$\sim$ 60 nm/min					

Table 4.23: Parameters used for dry etching of ZnO with an ECR system

sheet carrier density around  $10^{11}$  cm<sup>-3</sup>, and mobility around 70 - 80 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.

## 4.6.3 Optical Properties

The ideal refractive index for ZnO is given by Ref. (155), which is close to what as experimentally demonstrated as shown in the Figure 4.18. The data points were fitted to the Cauchy equation:

$$n = 1.5353872 + \frac{1.4938462}{\lambda^2} + \frac{1.1170864}{\lambda^4} \tag{4.6}$$

The refractive index can vary between 1.9 - 1.5 mainly dependent on the parameters set for the secondary source. The reason is because the secondary source can alter the composition of the films with oxygen atoms.

There are three absorption bands that make up the ZnO fingerprint, found in Figure 4.19. The first is located at 3244 cm<sup>-1</sup> due to O-H stretching vibrations. The formation occurs due to the presence of hydrogen impurities when the sample is exposed to atmosphere(156). Finally, another band that may appear is one located at 705 cm<sup>-1</sup>,



Figure 4.18: Dispersion of the refractive index of ZnO

and this is due to C-H bond bending. C-H bonds form in ZnO sputtered films due to the interaction between the hydrogen and carbon atoms, from the presence of a slight amount of  $CO_2$  in the primary ion source.

#### 4.6.4 Summary

Table 4.24 provides a summary of the general relationships between characterization and deposition parameters of ZnO. This information can be used to know what general parameters need to be adjusted in order to achieve specific material characteristics. A description of the notation is given in 4.1.4.



Figure 4.19: Absorption coefficient curve of ZnO

# 4.7 Zinc Selenide (ZnSe)

ZnSe is an attractive material because of being a direct wide bandgap material with a long transparency range. It is commonly used for windows and lenses, optical waveguides, quantum wells(157), luminescent devices, solar cells, and light emitting diodes. A wide bandgap in the material acts as an electrical barrier for electrons and holes, which leads to low surface recombination effects(158). It also has low absorption properties in the far-infrared and a relatively high refractive index that makes ZnSe a suitable device for IR optical coatings and optoelectronic devices.

The preparation of ZnSe is commonly performed by EBE(159) and CVD(160), and other techniques are typically not utilized due to the difficulties in working with the

Increasing	Deposition	RMS	Sheet	Refractive	Absorption
values in:	Rate	${\rm Roughness}$	Resistance	Index	Coefficient
Beam current	-↑	$\uparrow\downarrow$	$\downarrow\uparrow$	-	$\uparrow\downarrow$
Beam voltage	↑	↓-↑	$\downarrow$	-	$\uparrow\downarrow$
Dep. source Ar flow	-	$\uparrow\downarrow$	^-	↓-↑	$\downarrow\uparrow$
Assist source $O_2$ flow	↑	↓-↑	^-	↓-	$\downarrow$
Assist source power	↑	↑	$\uparrow\downarrow$	-↑	$\uparrow\downarrow$
Substrate temp	↑	$\downarrow\uparrow$	↓-	-	$\downarrow\uparrow$
Substrate angle	1	$\downarrow$	$\downarrow$	-	$\downarrow$

Table 4.24: Summary of the relationship between characterization results and deposition parameters of ZnO

material. The properties of bulk ZnSe are provided in Table 4.25(161)(162)(163).

Zinc Selenide (ZnSe)						
Crystal system	Cubic	Density	$5.42 \text{ g-cm}^3$			
(space group)	(Fm3m)	Bandgap	2.71  eV			
Solubility	0.001g:100g H <sub>2</sub> O	Poisson's ratio	0.30			
Elastic constants	$C_{11} = 0.8096$	Young's modulus	75.4 GPa			
	$C_{12} = 0.4881$	Bulk modulus	61.8 GPa			
	$C_{44} = 0.4405$	Rigidity modulus	29.1 GPa			
Bond strength	$170.7 \pm 25.9 \text{ mol-kJ}^{-1}$	Melting point	1790.0 K			
		Heat capacity	$0.339 \text{ J}\text{-g}^{-1}\text{K}^{-1}$			
	Thermal conductivity	$13.0 \text{ W-m}^{-1} \text{K}^{-1}$	-			

Table 4.25: Properties of ZnSe

## 4.7.1 Structural Properties

Typical deposition rate for ZnSe was found to vary between 3.5 to 5.5 nm/min. The variation was due to differences in the argon flow rates in the deposition source, RF power in the assistance source, ion beam voltage, and substrate-to-target angle. The

films showed a median roughness around 1.53 nm, with the minimum being 0.40 nm and maximum of 2.30 nm. The average grain size was measured to be around 13.0 nm wide and 3.0 nm tall. In general, the grains that make up the ZnSe material are much wider and shorter compared to the other oxide materials. This is most probable due to the surface tensions and slight preference of layer growth over island growth. Not only do the surface tensions affect the grain size, but also the adherence of the material. ZnSe is challenging with its adherence, as discussed in Section 8.4.1. In addition, the microstructure and grains of oxide materials are expected to have more favorable growth conditions because of the ability to use oxygen in the second source. In this case, only Ar was used. For etching, a  $C_6H_8O_7$  acid can be used with expected etch rates around 17 nm/min. Otherwise, ZnSe can be dry etched using the chemistry and parameters given in Table 4.26 and etch profiles are given in Figure 4.20.

Dry Etch Conditions of ZnSe					
Pressure	2 mTorr				
Microwave Power	$200 \mathrm{W}$				
RF Power	$200 \mathrm{W}$				
$CH_4$ Flow Rate	10  sccm				
$H_2$ Flow Rate	25  sccm				
Ar Flow Rate	5  sccm				
Substrate Temperature	30 °C				
Etch Rate	$\sim$ 50 nm/min				

Table 4.26: Parameters used for dry etching of ZnSe with an ECR system

There are two main difficulties with the deposition of ZnSe by IBSD that can become limiting factors: adherence and hardness. While IBSD has many advantages over other techniques, such as control in its adhesion, the highly energetic ions can pose problems.



Figure 4.20: SEM pictures of wet and dry etch profiles of ZnSe

ZnSe is a very soft material due to having a low bond strength and small hardness value, so it can be easily removed from the target source. There have many experimental issues with good adherence of the material to substrate, especially for some such as GaSb. If this is not carefully considered, peeling can occur and it can be observed how the film does not lack adherence to itself, but only lacks adherence to the substrate. One way of fixing this problem is by beginning the growth of ZnSe with an adhesive layer. One example would be a thin oxide layer that can be formed by introducing oxygen into the chamber prior and during the first few monolayers of deposition. Only a small amount of oxygen was found necessary in order to become effective. As mentioned earlier, ZnSe is a very soft material and the result of this is that it can be removed easily from the sample when the deposition conditions are too harsh. This poses a problem, especially when depositing different thin-film layers on top. One example is shown in Section 7.4.5, where the deposition of ZnO on top of ZnSe led to sputtering of the ZnSe layer and interfacial mixing. Oxide materials, in general, have a greater hardness. Typically the hardness of an oxide is around 500 - 600 kg/mm<sup>2</sup>, which is unlike ZnSe, with a hardness value around  $115 \text{ kg/mm^2}$ . Since ZnSe is one of the materials with lowest threshold energy, removal of the material can occur at energy values that would insufficient for sputtering of other materials. One solution to this was to deposit a protection layer on top of ZnSe by slowly ramping up the power of the ion-beam until the layer is thick enough for protection.

#### 4.7.2 Electrical Properties

The sheet resistance of the ZnSe deposited had a magnitude in the  $10^8 \Omega \backslash \Box$ , for a thickness of 100 nm. Further, the carrier concentration values were around  $10^{16} \text{ cm}^{-3}$ , sheet carrier density around  $10^{11} \text{ cm}^{-3}$ , and mobility around 30 - 40 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>

#### 4.7.3 **Optical Properties**

The range of refractive indices of ZnSe that was attainable was between 1.9 and 2.4, as shown in Figure 4.21. This is in good agreement with Ref. (164). Figure 4.7 shows the following fitted Cauchy equation:

$$n = 2.4038363 + \frac{1.3539869}{\lambda^2} + \frac{-1.1253286}{\lambda^4} \tag{4.7}$$

In this work, argon was used as the gas for the secondary assistance source. This gave the ZnSe films higher adatom mobilities, leading to lower film absorption and higher packing densities. There are two factors that need to be considered. The bombardment of the extra argon atoms can contribute to or induce preferential sputtering. For ZnSe, this means there is a higher probability that more selenium atoms will be sputtered off the substrate compared to the zinc atoms. A result of this can be a decrease in the refractive index due to the lower composition of selenium. The second possibility that needs to be considered is the trapping of argon gas atoms in the film. This can lead to undesirable properties such as higher compressive stress.



Figure 4.21: Dispersion of the refractive index of ZnSe

ZnSe is a good IR material due to its transparency, as shown in Figure 4.22. The material does not have many absorption bands present. The band located between 1660 - 1000 cm<sup>-1</sup> is apart of the material's fingerprint, and this is due to the vibration of the diatomic molecule(150). Another band is observed around 660 cm<sup>-1</sup> due to three-phonon absorption. Finally, the last band is located at 1503 cm<sup>-1</sup>, and this is due to the formation

of Zn-H bonds similar to ZnO films. The presence of residual hydrogen when exposed to air leads to the formation of the Zn-H and their vibrations cause this absorption to occur. One thing to note is that any impurity-induced vibrational modes(160) can make ZnSe an ineffective optical material by shifting its transparency edge.



Figure 4.22: Absorption coefficient curve of ZnSe

### 4.7.4 Summary

Table 4.27 provides a summary of the general relationships between characterization and deposition parameters of ZnSe. This information can be used to know what general parameters need to be adjusted in order to achieve specific material characteristics. A description of the notation is given in 4.1.4.

Increasing	Deposition	RMS	Refractive	Absorption
values in:	Rate	Roughness	Index	Coefficient
Beam current	$\uparrow\downarrow$	-	↓-	1
Beam voltage	-↑	-↓	↑	$\downarrow$
Dep. source Ar flow	Î	^-	↑	↑
Assist source Ar flow	$\downarrow$	↓-	-	$\downarrow\uparrow$
Assist source power	↑-	↑	-	$\downarrow\uparrow$
Substrate temp	$\downarrow$	$\uparrow$	↑	↑-
Substrate angle	Ť	↓-	↓ <b>-</b>	$\downarrow\uparrow$

Table 4.27: Summary of the relationship between characterization results and deposition parameters of ZnSe

# 4.8 Summary

One of the major advantages to using the IBSD system is the wide range of achievable material properties. The experimental ranges for the materials discussed in this chapter are given in Table 4.28.

	Deposition	RMS	Etch	Sheet	Refractive	Absorption	Bandgap
	Rate	Roughness	Rate	Resistance	Index	Bands	
	[nm/min]	[nm]	[nm/sec]	$[\Omega/\Box]$	Index	$[\mathrm{cm}^{-1}]$	[eV]
PbTe	4.6 - 12.3	0.5 - 5.9	4.3 - 6.2	$10^{3}$	4.6 - 5.6	$\begin{array}{c} 600,\ 740\\ 1500,\ 2613\end{array}$	0.3
$\mathrm{SiO}_2$	1.9 - 4.8	0.1 - 5.5	0.3 - 13.2	$10^{15}$	1.3 - 1.8	$\begin{array}{c} 461,\ 837\\ 1087 \end{array}$	8.0
$\mathrm{Si}_3\mathrm{N}_4$	3.2 - 5.1	0.1 - 0.3	1.1 - 4.5	$10^{13}$	1.9 - 2.2	493, 930	5.1
$\mathrm{TiO}_2$	1.6 - 4.0	2.0 - 7.4	18 - 22	$10^{11}$	2.0 - 2.8	526, 634, 2260	3.3
$Y_2O_3$	1.8 - 3.8	0.1 - 1.8	0.2 - 1	$10^{12}$	1.5 - 2.0	$715, 1470 \\ 4468$	5.2
ZnO	1.9 - 4.2	0.2 - 4.2	1 - 2.2	$10^{6}$	1.6 - 2.1	705, 3244	3.2
ZnSe	3.4 - 6.3	0.3 - 2.4	0.7 - 1.8	$10^{11}$	1.8 - 2.5	$\begin{array}{c} 660,\ 1210 \\ 1503 \end{array}$	3.1

Table 4.28: Summary of the characterization results and attainable ranges of all seven materials used in this work. The sheet resistance values are given for a film with thickness around 100 nm.

# **CHAPTER 5**

# Spatial Parameter Mapping

Predicting the exact behavior of the ions and atoms in the chamber is rather difficult because there are numerous processes ongoing simultaneously. In order to better understand what material properties are expected, spatial mapping of the parameters is necessary. One of the major advantages to the IBSD is the wide range of achievable material characteristics and the ability to fine tune those characteristics.

This section discusses the main system parameters in the IBSD system and the influence it has on the material characteristics. The role of each parameter is discussed, and can be related to the models and equations provided in Section 2.3. It must be noted that the behavior of the particles in the chamber and the characteristics of the deposited materials can vary quite a bit dependent on the condition of the chamber and the target. For example, deposition with an eroded target can lead to changes such as film stoichiometry(123). Details on proper pre-deposition conditions are given in Section 2.2. Since the film properties are so sensitive, the information provided in this chapter should be used as a general guideline, and it is always recommended to use experimental results.

## 5.1 Primary Deposition Ion Source Parameters

The purpose of the primary deposition ion source is to bombard the target to remove the material and deposit onto the substrate. The main parameters that are important for this is the beam current, beam voltage, and bombarding gas properties. Each one will be discussed in this section along with their relationships to material characteristics.

#### 5.1.1 Ion Beam Current

The ion beam current is the flow rate of the ions that are extracted from the primary deposition ion source and used in the bombardment of the target material. The ions have a velocity  $v_0$ , related to the ion-beam current, and this value affects the momentum of the target atoms after the collisions occur, as discussed in Section 2.3.3. The current is related to both the ion fluency and the ion-to-atom ratio. The ion fluency is the ratio of the number of ions impinging on the substrate per unit time to the number of atoms remaining on the substrate, typically stated in units of  $J/cm^2$ . It is a very hard parameter to determine accurately, but there exist tools, such as a Faraday cup, that can be used. The ion-to-atom ratio I/A can be approximated by taking the ratio of the ion-beam current to the deposition rate or sputtering yield. While other parameters such as beam voltage, chamber pressure, and assist source RF power can modify the I/A ratio, the

beam current is the dominant parameter.

#### Deposition rate

In general for all materials, the deposition rate increased with beam current similar to observations made in Ref. (165). A linear relationship to the sputtering yield was observed for some materials, such as SiO<sub>2</sub>, as shown in Figure 5.1. This trend is expected from Sigmund's model(7), and, with all other parameters fixed, the model is followed exactly. However as the current increases to higher values, resputtering can begin to dominate. This leads to a loss of already-deposited material on the substrate, causing the experimental deposition rate to deviate from Sigmund's model. If the reason for the loss in atoms is not resputtering, it is because the higher energy of the incoming ion will cause the target atoms to have larger scattering angles. This results in an overall scattering farther away from the substrate. This was shown in Figure 2.4 of Section 2.3.2. Deviations were exhibited with  $Y_2O_3$ , ZnSe, ZnO, and SiO<sub>2</sub>, listed in the order of turning points from lower to higher. For Si<sub>3</sub>N<sub>4</sub>, TiO<sub>2</sub>, and PbTe, only a linear trend was observed. These materials have the highest threshold energy values and so currents greater than the maximum need to be utilized in order to reach the highest deposition rate.

#### Surface morphology

The ion-beam current demonstrated relatively no effect the surface morphology of  $SiO_2$ ,  $Si_3N_4$ , PbTe, and  $Y_2O_3$ . However, it did improve for  $TiO_2$ , ZnO, and ZnSe once a certain current value was reached, similar to Ref. (166). This is because the three materials have



Figure 5.1: Deposition rate relationship with the deposition source ion-beam current and voltage. This is compared to the sputtering yield predicted by Sigmund's model.

the highest energy mass transfer, so the ion-beam current is more effective in providing it with a slight bit more of energy. Since the extra energy is minimal, it will not necessarily remove the atom, but instead allow it to mobilize along the surface and smoothen it out.

#### Film density

The film surface is related to the density of the films, this explains why high I/A values leads to both decreased void volume(167) and smoother surface. The increased density with higher beam current values was observed in the experimental tests, but up to a certain value where higher than this leads to a decrease due to reaching a limit where the maximum number of voids can be filled. Increasing the I/A above the limit will result in other processes dominating and creating unwanted effects such as structural disorder and/or creation of defects. A few other effects of this is poor interfacial roughness(168) and decreased crystallinity.

#### Sheet resistance

The influence of the beam current on the resistance or insulating properties of the materials results in generally higher values and with only slight changes for some materials. One example is ZnO where minimal change in resistance was observed, and this was also true with Ref. (139). On the other hand, SiO<sub>2</sub> showed a large effect, where the resistance was  $R_s = 4.44 \times 10^9 \ \Omega \square$  at  $I_b = 86 \text{ mA}$  and  $1.45 \times 10^{12} \ \Omega \square$  at  $I_b = 170 \text{ mA}$ . The improved resistance is due to the higher film density, which leads to fewer voids and prevents conduction paths between grains.

#### Refractive index

A change in refractive index with varying beam currents was observed to occur with  $SiO_2$ , ZnO, ZnSe, and  $Y_2O_3$  only. For increasing beam currents, a jump in value initially occurred, then a steady decrease in refractive index value was exhibited.  $SiO_2$  showed similar behavior but without the initial jump. The reason why a change in the refractive index occurs is due to preferential sputtering, where  $SiO_2$ , ZnO, and  $Y_2O_3$  had a higher amount of  $O_2$  and ZnSe had a higher amount of Se, both explaining the changes. These four materials are unique from the others in that their threshold energy values were the lowest. Since the energy was not high enough, this caused no preferential sputtering with

the other materials. The other materials had a high enough energy, so changes in stoichiometry have been demonstrated (169)(170). The discussion on preferential sputtering given in Section 5.2.2 indicates that the preference occurs due to energy transfer becoming more effective with lighter masses than heavier ones. However, there may be other sources causing this preference such as ionic charge, as indicated by Ref. (171).

#### Absorption coefficient

The beam current did not show a significant effect on the absorption coefficient except for ZnSe. ZnSe is unique for all others because it is the material with highest energy mass transfer. The absorption coefficient of ZnSe films became significantly higher when the beam current value was increased beyond a certain point of around I = 120 mA. This is because the structural disorder and defects led to light trapping between grains, accounting for the loss in power and intensity.

#### Bandgap

Any slight modification in bandgap can be found due to changes in the carrier concentration, where higher current values has been observed to causes a shift towards higher bandgap values(139). ZnO showed a shift towards higher values up until a beam current of 110 mA and 140 mA for ZnSe. Any higher of a value than this would cause a shift to lower bandgap values. This is different from TiO<sub>2</sub> where a close-to-linear shift to lower values occurred and their turning point was higher than the maximum. A similar relationship was observed with Y<sub>2</sub>O<sub>3</sub>, whose direction of shift was opposed for I<sub>b</sub> = 130 mA
and current values greater than this.

# 5.1.2 Ion Beam Voltage

The deposition source ion beam voltage plays a role in the properties of the films because it affects the ion energy. The voltage determines how much of the current is extracted from the source(14), affecting factors such as surface morphology and film microstructure. The ion energy at the target surface is determined by the potential difference between the plasma potential and the ion energy right after emergence from the ion source. In this case, the target was grounded, so the potential difference is equal to the total voltage  $(V_t = V_D - V_A)$ . Therefore, the energy that the target sees is equal to the different in applied and accelerator voltage. Slight variations in the plasma voltage may occur due to the peak-to-peak voltage measured at the substrate, equal to  $eV_{pp}(172)$ ; this is only valid for negative ions that are fully accelerated. For recoil argon atoms, a different energy can be expected equal to(105):

$$E_{Ar} = \frac{(M_{target} - M_{Ar})^2}{(M_{target} + M_{Ar})^2} V$$
(5.1)

### Deposition rate

The relationship between the ion beam voltage and the deposition rate is similar to the change seen with the ion-beam current except a more dramatic difference is seen here. For all the materials, the deposition rate showed a consistent increase with higher voltage values(173). Then at voltages nearing the maximum, the deposition rate decreases most

likely due to resputtering(174).

### Surface morphology

The ion-beam voltage showed a general decrease in the RMS roughness for higher values. There was an insignificant change with  $SiO_2$ ,  $Si_3N_4$ ,  $Y_2O_3$ , and ZnSe. For ZnO and TiO<sub>2</sub>, up to 2.8 times decrease in RMS roughness occurred when changing the voltage from 800 V to 975 V due to the increased amount of energy to the atoms(175)(174)(172). The extra energy allows the instigation of single-knock on sputtering, as described in Section 2.3.4, explaining the surface morphology change. The explanation for the impact on ZnO and TiO<sub>2</sub> and not others is shown in Table 2.4, where the materials with highest energy mass transfer were affected. On the other hand, PbTe showed the opposite relationship where the roughness worsened with higher beam voltages. This can be attributed to the higher nuclear collision cross-section of PbTe, which can lead to structural disorder and damage.

#### Film density

Higher beam voltage values lead to higher packing densities because the ions have more energy by the time they reach the substrate, and therefore have a higher chance of being able to mobilize along the surface to fill voids. Using chemical acid etching, a linearly decreasing relationship exists between the etching rates and the voltage. This is similar to Ref. (172), except they observed a saturation in density for very high voltage values

### Sheet resistance

The relationship between sheet resistance and beam voltage is generally the same as the relationship between sheet resistance and beam current. A higher voltage led to higher sheet resistance values because the more energetic adatoms leads to altering of the microstructure. However, this is true up until a certain voltage value being 800 V for ZnO, 870 V for SiO<sub>2</sub>, and 930 V for Si<sub>3</sub>N<sub>4</sub>. All other materials such as Y<sub>2</sub>O<sub>3</sub> did not have a roll-over point.

### Refractive index

Higher beam voltages caused higher refractive indices for ZnSe, SiO<sub>2</sub>, and PbTe and no effect on the other four materials. This relationship was also observed when changing the beam current, affecting only those materials with low threshold energy values. However, there was one slight difference in the refractive index of SiO<sub>2</sub>. It increased with beam voltage, instead of decreasing like it did with beam currents. Further PbTe also showed an increase in the refractive index, followed by an asymptotic decrease, similar to what was observed in Ref. (172). The reason for this change in behavior is unknown and needs further investigation.

### Absorption coefficient

The absorption coefficient changed for different beam voltages showing a steady increase with  $Si_3N_4$  and PbTe, unique due to its low energy mass transfer function. Also, a steady decrease with TiO<sub>2</sub> and ZnO, unique to its high energy mass transfer function. Absorption of light can occur when there is light trapped between grains. If the atoms do not have sufficient energy to fill in voids, this will lead to large spacing between grains or pores. This explains why  $Si_3N_4$  and PbTe are negatively affected, since they have the lowest energy mass transfer. Additionally, since TiO<sub>2</sub> and ZnO have the highest energy mass transfer values, they can use the extra energy to fill the voids and avoid light trapping.

### Bandgap

The bandgap of the materials were found to show a general shift towards lower values when higher beam voltage values were used. All shifts occurred linearly with about the same rate of about  $\Delta E_g = -7.1 \text{ eV-V}^{-1}$ . This may be due to the crystalline state of the material(176)(177).

### 5.1.3 Accelerator Voltage

The accelerator voltage is the voltage applied to the second grid used to accelerate the ions. Opposite from the applied voltage, the accelerator is a negative potential value and helps to prevent electrons from traveling back into the source. In addition to affecting the total voltage of the ions coming from the source, the accelerator voltage affects the beam divergence. In general, a larger beam divergence is expected for lower accelerator voltages. One might expect to be able to achieve the same characteristics for two situations with the same total voltage, but this is not the case for different accelerator voltages which has a large role in the current density between two grids. The current density can be given as(3):

$$j = \left(\frac{4\epsilon_0}{9}\right) \left(\frac{2e}{m}\right)^{1/2} \frac{V_t^{3/2}}{l^2} \tag{5.2}$$

where l is the spacing between the grids, and e/m is the charge to mass ratio of the particles emitted. The current density and acceleration modifies the relative fraction of scattered  $Ar^+$  ions.

There are a few differences that were seen when adjusting  $V_a$ . The first was surface morphology and AFM scans are shown in Figure 5.2. Lower transmittance, higher reflectance, a slight shift in the quarter-wave wavelength was also observed in Figure 5.3 and Figure 5.4.



Figure 5.2: AFM scans of ZnO samples with different accelerator voltages

# 5.1.4 Argon Gas Flow Rate

The argon gas flow rate controls the flux of the ions reaching the target. This parameter essentially changes the discharge voltage, which is related to the potential difference between the target and substrate. For higher discharge voltages, the ions/atoms will experience a higher acceleration when traveling from target to substrate.



Figure 5.3: Transmittance of ZnO samples with different accelerator voltages



Figure 5.4: Reflectance of ZnO samples with different accelerator voltages

### Deposition rate

The deposition rate did not show any significant changes for  $Y_2O_3$ , ZnO, and SiO<sub>2</sub>. A slow and steady increase occurs with TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and ZnSe. This is similar to the behavior observed in Ref. (148). PbTe showed a different relationship with a large drop in rate at lower flow rates and then saturation occurred when the rate was increased to higher values.

### Surface morphology

The RMS roughness value showed virtually no change with  $Y_2O_3$ ,  $Si_3N_4$ , and  $SiO_2$ . All other materials experienced an initial decrease in roughness when increasing the argon flow rate in the deposition source. The smoother surface can be attributed to smaller crystal sizes(10). After this, a minimum was reached, and the roughness then increased. Typically the final roughness value was the maximum at the highest allowable flow rate (20 sccm), but not as large a number as the roughness at the very low flow rates (5 sccm).

### Sheet resistance

The resistance of the materials showed an increase in value going from very low flow rates to a higher flow rate. A maximum in the resistance value was reached, and then the resistance would decrease at a certain point. The point where this occurs was found to be 8 sccm for  $Y_2O_3$  and 11 sccm for ZnO. The change in resistance was minimal for all materials such as  $Si_3N_4$  and  $SiO_2$ .

### Refractive index

A change in refractive index was only seen with  $SiO_2$  and ZnSe. As the flow rate became higher, the refractive index for both materials gradually increased and then saturated in value for the very high rates. This is the same relationship observed by Ref. (10), where a lower transmittance occurred with lower flow rates and high reflectance for higher flow rates.

### Absorption coefficient

While the flow rate did not have an effect on the refractive index of all materials, it did have an effect on their absorption coefficient values. Similar to the refractive index change,  $SiO_2$  and ZnSe, along with  $Si_3N_4$  showed a continual increase in value. On the other hand, the other materials showed the following: an initial decrease, a minimum value was reached, and finally an increase occurred for the higher flow rate values.

### Bandgap

Generally, an insignificant change in value occurred when the argon flow rate in the deposition source was observed. This is different from Ref. (10) who showed a slightly higher  $E_g$  with flow rate.

# 5.1.5 Oxygen Gas

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The utilization of oxygen in the primary source can be beneficial for certain situations. One situation is reactive sputtering where the oxygen gas can be used to oxidize the target. Without this oxidation, the deposition becomes metal sputtering instead of the oxide desired.

### Deposition rate, Surface morphology, and Film density

There are a few differences in the material properties with and without oxygen in the deposition source. The first is deposition rate, where the rate is higher when  $O_2$  is used. This can be explained due to the greater number of oxygen atoms. Another difference is the morphology shown in Figure 5.5. The RMS roughness differs significantly with values being around 2-3 times higher. In addition to worsening the surface roughness, the added gas has an effect in making the films more porous. This leads to higher etch rates observed being more than double in value.



Figure 5.5: Side-by-side comparison of the AFM scans for  $TiO_2$  samples with different oxygen gas flow rates, (a) 1 sccm and (b) 2 sccm, in the primary ion source

### Sheet resistance

The electrical properties are also affected with sheet resistance values that were much higher for the sample without oxygen. This can explained due to the microstructure and its relationship to conduction paths.

### Refractive index and Absorption coefficient

For the optical properties, the refractive index is lower for the sample with oxygen gas. This can be expected since there is a higher amount of oxygen incorporated into the films. In addition, the absorption coefficient is much worse. The oxygen atoms interfere with the ions that reach the target and the extra flux will lead to less energy. This explains the higher surface roughness and higher void volume, discussed earlier. A result of this is a higher absorption coefficient.

# 5.1.6 RF Power

For the system used in this work, the RF power was not directly controllable. However, the value could be altered by adjusting other parameters. The relationship to the ion beam current is shown in Figure 5.6, beam voltage in Figure 5.7, and argon flow rate in Figure 5.8. With increasing RF power, the following should be expected: higher deposition rate, lower RMS roughness, higher film density, higher film stress, worse interface quality, higher sheet resistance values, higher refractive indices, and lower absorption coefficient (165)(178)(149)(15).



Figure 5.6: Relationship between RF power with the deposition ion source and beam current. A general increase in RF is observed with beam current

# 5.2 Secondary Assist Ion Source Parameters

The system is equipped with a second ion-source, which is directed towards the substrate and has a purpose of assisting in achieving high-quality films. The utilization of the secondary source can lead to major improvements in the characteristics including stoichiometry, density, refractive index, film absorption(98), and adherence(166). For structural properties, the assist source has a large impact on the microstructure and growth of the first initial layers. Since the current density from this source is very low, virtually no surface damage can be attributed to it. This is verified in Section 2.2.2. For electrical properties, reduced leakage current can be achieved due to the enhanced adatom mobil-



Figure 5.7: Relationship between RF power with the deposition ion source and beam voltage. A general decrease in RF is observed with beam voltage

ities allowing for more favorable energy sites to become occupied. Finally, for optical properties, the films' refractive index can be modified with extra supplement of oxygen or nitrogen atoms. The atoms can compensate for any loss of atoms due to preferential sputtering and can modify the film's refractive index. This can be observed with Figure 5.9, Figure 5.10, and Figure 5.11. The utilization of the secondary source shows a significantly higher transmittance, most likely attributed to lower film absorption. Two main parameters that can be adjusted with the secondary source are the plasma power and gas flow rates; each one will be discussed in this section.



Figure 5.8: Relationship between RF power with the deposition ion source and argon flow rates. The RF power decreases with argon flow rates

# 5.2.1 RF Power

The RF power in the secondary source is effective in the same means as it is with the primary source. They both supply energy, however the primary source supplies energy to that ions reaching the target. Instead, the RF power in the secondary source supplies extra energy to the already-deposited atoms that have landed on the substrate. The effects will be discussed here.

### Deposition rate

The deposition rate for all the materials increased with higher RF powers. The change was more dramatic in some (PbTe, ZnO,  $Y_2O_3$ , and  $Si_3N_4$ ) while other materials (ZnSe,



Figure 5.9: FTIR measured transmittance of ZnO samples deposited both without and with utilization of the assist RF source

 $TiO_2$ , and  $SiO_2$ ) had an insignificant change. The reason for the increase in deposition rate is because, for slight increments at low powers, the particles have a higher probability of landing on the surface(165)(148)(127)(15)(149). Once the RF power got to be too high, the deposition rate did not increase.

### Surface morphology

The RMS roughness relationship with the power differs depending on the energy mass transfer with the gas used in the secondary source. In general, the surface morphology showed greater improvement when the energy mass transfer was high. This was observed with TiO<sub>2</sub> and SiO<sub>2</sub> using O<sub>2</sub> assistance. The improvement is expected since the energy transfer is effective and gives energy to adatoms(179)(180). The extra energy stimulates



Figure 5.10: FTIR measured reflectance of ZnO samples deposited both without and with utilization of the assist RF source

the bridging between neighboring grains, filling in-between voids, and promoting good grain growth. Additionally, the morphology of  $Y_2O_3$  and ZnSe worsened with higher RF powers since their energy mass transfer with either  $O_2$  atoms or  $N_2$  atoms is low. In this case, the energy mass transfer is insufficient to provide energy to the already-deposited atoms. PbTe and ZnO exhibited behaviors where an initial decrease in roughness occurred, and then at a median flow rate, the roughness starts to increase. These two materials are different in having a higher susceptibility due to its short penetration length. These negative changes were due to structural disorder and defect generation(15).

### Sheet resistance

 $\rm Si_3N_4$  showed an increase in sheet resistance value from 0.401 x 10^{13} \ \Omega \backslash \Box to 5.087 x 10^{13}



Figure 5.11: Absorption coefficient of ZnO samples deposited both without and with utilization of the assist RF source

 $\Omega \setminus \Box$  within the range of 200 W to 600 W. Whereas  $Y_2O_3$  showed a decrease in the sheet resistance from 3.19 x 10<sup>11</sup>  $\Omega \setminus \Box$  at RF P = 200 W to 0.332 x 10<sup>11</sup>  $\Omega \setminus \Box$  at RF P = 600 W. A decrease in resistance also occurred with ZnO from 8.64 x 10<sup>5</sup>  $\Omega \setminus \Box$  at RF P = 400 W to 0.84 x 10<sup>5</sup>  $\Omega \setminus \Box$  at RF P = 400 W, but this relationship was only true for power values greater than a certain turning point, in this case 400 W.

#### Refractive index

The refractive index was relatively unaffected by the RF powers at low values. Once the power was increased to higher values, the refractive index of ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> increased, similar to Ref. (178). This is because Zn, Ti, and Si have the highest energy mass transfer ratios with  $O_2$ , which makes the amount of preferentially sputtering to be lower and less  $O_2$  rich.

#### Absorption coefficient

There was a very slight decrease in the absorption coefficient values for ZnSe, ZnO, and PbTe. This is different from TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and SiO<sub>2</sub> which had a very slow and steady increase.  $Y_2O_3$  showed an initial increase, and then decreased at higher powers. The commonality of ZnSe, ZnO, and PbTe are that these materials have the highest densities. There are many effects this has, one example is that Ar gas atoms have a higher probability of being trapped within the material. These atoms are essentially voids that trap light and reduce the overall intensity emitted. This behavior is somewhat similar from what was observed in Ref. (178), where no change in optical properties were observed.

### Bandgap

The RF power in the secondary source was found to have had only a slight amount of influence with bandgap on the materials. One exception is  $Y_2O_3$ , where an exponentially decreasing relationship occurred(176). ZnO, ZnSe, and TiO<sub>2</sub> showed a slight increase when the beam RF power is changed from 200 W to 300 W, however values higher than this led to no changes.

### 5.2.2 Gas Flow Rates

In addition to the power of the secondary source, the gaseous flow rates are very important in influencing the properties of the films. Preferential sputtering is the process of preferentially removing one type of atom over another in the target material. While it has been postulated that the preference is dependent on the electronic processes in the target material(171), this work has followed the concept that the amount of preferential sputtering depends on the mass and surface binding energies of the atoms(181).

$$\left(\frac{X_1}{X_2}^{s}\right) = \left(\frac{X_1}{X_2}^{b}\right) \sqrt{\frac{A_1}{A_2}} exp\left(\frac{U_1 - U_2}{kT}\right)$$
(5.3)

where  $A_1$ ,  $A_2$  are the atomic masses and  $U_1$ ,  $U_2$  are the respective surface binding energy values of the compound target material  $X_1Y_2$ . The amount of preferential sputtering can be found by taking the ratio of Eq. 5.3. If the ratio is greater than one, than the first atom has a higher probability of being removed from the target. Typically, this will lead to the sample being rich with the first atom and deficient of the second.

There are many uses for the reactive gas in the secondary source. One reason is to compensate for any loss during the sputtering process due to preferential sputtering. A sufficient amount may be needed to achieve the desire stoichiometry. However a larger amount than necessary can lead to issues such as the formation of unwanted oxide layers for oxygen assistance. One problem with argon assistance is that too high a flow rate can lead to trapping of gaseous atoms in the films, contributing to compressive stress. Otherwise, the non-ideal flow rate can lead to abnormal grain growth, modified microstructure, and alterations with the preferred orientation of the film growth(182).

### Deposition rate

With a reactive gas sent to the substrate through the secondary source,  $SiO_2$ ,  $TiO_2$ ,

ZnO,  $Y_2O_3$ , and  $Si_3N_4$  all showed a decrease in its deposition rate with higher gas flow rates(9)(141)(183). On the other hand, ZnSe and PbTe showed an increase in the deposition rate. These two materials are unique in that the assistance gas used is not a component of the target material. For both PbTe,  $N_2$  was used and for ZnSe, Ar was used. The choice of gas was made depending on the absorption coefficient. For different objectives, other gases may be more appropriate. For example, utilization of argon in ZnSe films is typically not done for thick layers due to its higher amount compressive stress. In the case of ZnSe, since argon is an inert gas, no reaction occurs with the material; however the increased deposition rate is due to the extra argon atoms that have become trapped in the film.

### Surface morphology

The flow rates of the gas through the assistance source did not have any effect on the surface morphology of  $Y_2O_3$ , SiO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub>. TiO<sub>2</sub> and ZnO showed a decrease in roughness with a minimum occurring at 10 sccm for ZnO(165)(182) and 14 sccm for TiO<sub>2</sub>(9). Following this, both materials showed an increase in roughness back to the same value when a flow rate of 5 sccm was used. The AFM scans of five samples with different O<sub>2</sub> flow rates are shown in Figure 5.12 for TiO<sub>2</sub>. Observation of the grain size, shape, and spacing shows a significant change with the flow rates; this can be attributed to a change in the nucleation of the grains. The grain growth is what caused the increase in roughness with ZnSe and PbTe.



Figure 5.12: AFM scans of five TiO<sub>2</sub> samples showing the change in morphology with higher O<sub>2</sub> flow rates in the secondary assistance source. The RMS roughness decreases with higher flow rates and a spike is observed with O<sub>2</sub> = 20 sccm

### Film density

The effect of higher flow rates on the density is similar to what was observed with the surface morphology. The films were more densely packed with higher flow rates, but only up until a certain point where other processes then dominated. Too high of a flow rate led to an impingement flux that induced resputtering, and therefore lower packing densities(9).

### Sheet resistance

The sheet resistance follows the same trend as the roughness and packing density. For oxides, a slight amount of oxygen incorporated in the films caused a jump in the resistance values (182)(102), and it increased due to the change in stoichiometry. This occurred only up until a certain point where structural issues led to the worsening of the electrical properties. This value was around 7 sccm for ZnO and 10 sccm for Y<sub>2</sub>O<sub>3</sub>.

### Refractive index

The films showed a decrease in refractive index(149)(184) as the assistance gas flow rate was increased. The reason why this occurred is because there is a larger amount of incorporation of  $O_2/N_2$  in the films(183). This is similar to what was observed in Ref. (15), where the lower refractive index led to a smaller mismatch in refractive indices and therefore caused higher transmittance values.

### Absorption coefficient

The absorption coefficient decreased for ZnO,  $Y_2O_3$ , and TiO<sub>2</sub> when using higher flow rates through the secondary source(185). The lower absorption coefficient for the three materials is related to the RMS roughness, where the smoother surface led to less light trapping. This is different from PbTe, SiO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub> which showed a gradual increase in value. This increase is demonstrated in Figure 5.13 for the absorption coefficient of SiO<sub>2</sub>.

### Bandgap

The bandgap of the materials was influenced by the flux of gas atoms in the secondary source only at high flow rates, where values greater than 14 sccm led to a change in bandgap between  $\Delta E_g = 0.02 - 0.03 \text{ eV-sccm}^{-1}$  for TiO<sub>2</sub>, ZnSe and Y<sub>2</sub>O<sub>3</sub>. Further, a slightly greater amount of difference is seen with ZnO of about  $\Delta E_g = 0.04 \text{ eV-sccm}^{-1}$ . This change is attributed to the oxygen vacancies in the material(176)(186)(187), being the same reason why the refractive index changed.



Figure 5.13: Change in extinction coefficient for different oxygen partial pressures in the chamber during the deposition of  $SiO_2$ . No significant shift in the position has been observed, but changes in intensity are apparent

# 5.3 Chamber Parameters

While the actions of the particles inside the ion sources, between the grids, and right when they are extracted from the ion source are important, the conditions of the chamber are equally important. Other influences such as the substrate temperature, substrate angle, chamber pressure, and HPN current can be used to enhance the properties further with better sticking coefficients, lower compressive stress, and lower target charging. This section serves to prove this.

## 5.3.1 Substrate Temperature

In the IBSD system, the role of the increased temperature is to enhance the properties of the films by providing the atoms with extra energy in the form of heat. This is an added benefit, unlike PECVD, where a high substrate temperature is an absolute necessity in order to carry out the proper reactions. In addition to the intentional electronic heating supplied to the substrate, the substrate surface temperature will be higher due to bombardment of the ions. The amount of increase is highly dependent on the deposition parameters, the target material, and the gases used.

### Deposition rate

The deposition rate of all materials became lower in value when the substrate temperature was higher. This occurs due to the higher diffusion of the atoms. Since the adatoms now have a higher probability of filling voids, the end result is a thinner film. The effects were more prominent with  $SiO_2$ ,  $Si_3N_4$ ,  $TiO_2$ , and  $Y_2O_3$ , which are the materials with smaller density. Since their density is smaller, the thermally supplied energy allows them to mobilize easier.

### Surface morphology

Similar to the deposition rate, the change in RMS roughness was the same for all materials. The largest effect occurred with TiO<sub>2</sub> and PbTe with maximum differences of  $\Delta$ RMS = 5.12 nm and  $\Delta$ RMS = 3.96 nm. The reason is because all other materials already have a relatively low surface morphology, so little change was observed.

### Film density

In general, the film density became higher with substrate temperatures, similar to what was observed in Ref. (112). This relationship occurs for the same reason the deposition rate decreases where the probability of voids becoming filled is higher. The density showed to have a profound impact on the etching rate, which became nearly half in value comparing depositions at 30 °C and 250 °C. However, this is different from Ref. (178), which showed slightly lower densities with higher substrate temperatures for ZnO.

### Sheet resistance

Due to the higher film density, a higher sheet resistance was observed with higher substrate temperatures. The fewer number of conduction paths in-between grains led to more insulating films, similar to what was observed in Ref. (3). This was true for  $Y_2O_3$ , but the behavior of ZnO varied dependent on the actual temperature value. The behavior was similar to reports in Ref. (140), who showed lower resistivity, increased mobility, and lower potential barrier heights with higher temperature deposition of ZnO up to 200 °C. In this work, the temperature threshold was 130 °C for ZnO and 150 °C for Si<sub>3</sub>N<sub>4</sub>.

### Refractive index

The refractive indices of the materials were found to be relatively unaffected by the substrate temperature.  $SiO_2$ ,  $TiO_2$ , and ZnSe show a slight increase, but the changes

were rather insignificant.  $Y_2O_3$  showed the most prominent change, similar to reports given by Refs. (178) and (2). This is opposite from Ref. (9), who showed a decrease in the refractive index with higher substrate temperatures.

### Absorption coefficient

The absorption coefficient changed for all materials when the substrate temperature was varied. A slight and gradual increase was observed with  $Si_3N_4$ , ZnSe, SiO<sub>2</sub> and PbTe. This is different from TiO<sub>2</sub>, ZnO, and Y<sub>2</sub>O<sub>3</sub>. All three of these materials exhibited a decrease in absorption(140) and then a minimal value was reached where any temperature higher than this leads to higher values. For all materials, the increase in absorption is due to light trapping that occurs due to nucleation of islands with higher temperatures.

### Bandgap

The amount of change in bandgap due to different substrate temperatures during the deposition process was significant. For example, the range of bandgap values was 2.46 eV at T = 30 °C to 2.72 eV at T = 350 °C for ZnSe. This relationship is, however, opposite from ZnO which changed from 3.5 eV to 3.37 eV for the same temperature range. A similar relationship was observed with TiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>.

### 5.3.2 Substrate Angle

The substrate angle is the difference in angle between the secondary source and substrate referenced from normal. Since the substrate faces both the target and the secondary source, any slight changes in the angle will modify influences from both sources.

### Deposition rate

The deposition rate increased for all materials when the substrate angle was higher, meaning the angle between the target and substrate is higher. This rate followed as expected with an increase from more atoms reaching the substrate due to the cosine law.

### RMS roughness

The RMS roughness decreased slightly with higher angles for ZnSe, PbTe, ZnO,  $Y_2O_3$ , and  $Si_3N_4$ .  $SiO_2$  showed the same trend, but this was only until a certain point where the surface gets rougher when the angle nears closer to the target so that their normal incidence coincides. While the surface morphology difference was negligible for  $SiO_2$ , the change in energy of the ions and atoms did change the etch rate. There was a 2.8 times of a difference with the rate being 1.8 nm/sec when angled towards the secondary source at an angle of 15° to 4.0 nm/sec when angled towards the target source at an angle of 35°. If the angle is too low, the substrate predominantly faces the secondary source, and the transfer of momentum is such that linear cascade occurs. If the substrate is angled closer to the target, the sputtering mechanism is most likely to be single knock-on which will help to smoothen out the surface.

### Film density

The film density got lower when the substrate-to-target angle was higher in value. The

reason is because with higher angles, the substrate is facing more towards the target than the secondary source. Since on the major roles of the secondary source is to make the films more densely packed, the impact becomes less and less as the substrate is angled away.

#### Sheet resistance

The change in resistance varied for the different materials.  $Y_2O_3$  showed an unnoticeable difference in its electrical properties. On the other hand, ZnO showed a rate change of about  $\Delta R_s = 0.4 \ \Omega \setminus \Box$  per degree and  $Si_3N_4$  showed a rate change of about  $\Delta R_s = 0.67 \ \Omega \setminus \Box$  per degree. For both materials, the largest change occurred when the substrate is facing dominantly towards the secondary source.

### Refractive index

Any changes in the substrate angle appeared to lead to no changes in the refractive index for any of the materials. SiO<sub>2</sub> showed a range in values between n = 1.46 - 1.47, Si<sub>3</sub>N<sub>4</sub> between n = 2.02 - 2.05, TiO<sub>2</sub> between n = 2.12 - 2.10, Y<sub>2</sub>O<sub>3</sub> between n = 1.72 - 1.75, and ZnO between n = 1.87 - 1.9. ZnSe showed the highest range of attainable values (n = 2.26 - 2.42) with adjustments in angle and PbTe showed relatively no change at all.

### Absorption coefficient

The absorption coefficient decreased for all materials with higher angles.  $Y_2O_3$ ,  $SiO_2$ , and  $Si_3N_4$  also showed a very slight increase when the angle is close to normal incidence with

the target.

### Bandgap

With the substrate-to-secondary source angle varying from 15 °C to 35 °C, the bandgap changed only for  $Y_2O_3$  and ZnSe. An average change of about -0.055 eV-°C<sup>-1</sup> for  $Y_2O_3$ over the entire span of angles, and a slightly higher rate of about -0.06 eV-°C<sup>-1</sup> for ZnSe up until 25 °C can be expected. For angles where the substrate faces more towards the target, the ZnSe material will have a higher bandgap.

## 5.3.3 Chamber Pressure

The chamber pressure in the system used for this work can be changed by using the inert gases (175). One example is oxygen where a higher flow rate will lead to higher sputtering pressures. Further, higher beam currents and/or lower beam voltages have been found to increase the pressure. The pressure inside the chamber affects many different processes. One major one is the mean free path length of the particles. A higher pressure will lead to lower mean free path lengths, so the likelihood for a collision to occur is higher. The number of collisions is equal to the chamber pressure as(105):

$$N = \frac{dp_{tot}\sigma}{k_b T} \tag{5.4}$$

where  $dp_{tot}$  is the chamber pressure,  $\sigma$  is the collision cross-section, and T is the chamber temperature. Since atoms lose energy with each collision, the greater number of collisions will lead to a higher energy loss by the time the atoms reach the substrate. One example influence is the pressure involving the crystalline nature, where in general a more crystalline material is deposited at lower pressures due to the lower surface diffusion from the frequency of collisions(188) and the lower energy loss due to this. This can also be a method in promoting a higher incorporation of gases into the films.

### Deposition rate

As predicted, the relationship between chamber pressure and deposition rates was higher values. This was true up until a certain point, and any higher decreased the rates(127)(115). This was the case for TiO<sub>2</sub> and ZnO. However, a separate trend occurred in SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>. Materials such as ZnSe, Y<sub>2</sub>O<sub>3</sub>, and PbTe showed no significant changes.

### Surface morphology

The surface morphology exhibited changes in a few materials; those that were not affected by the pressure include  $Y_2O_3$ ,  $Si_3N_4$ , PbTe, and  $SiO_2$ . ZnO shows improved surface morphology, while both ZnSe and TiO<sub>2</sub> show worsening. The samples were rougher due to the change in energy of the negative ions and recoil atoms(105).

### Film density

The influence of the pressure on the change in energy of the negative ions and recoil atoms led to higher void volumes and faster etch rates. The surface morphology, film density, and sheet resistance were all affected by this due to their relationships with each other.

### Sheet resistance

For electrical properties, higher sputtering pressures led to a decrease the electrical resistivity (173). This is true up until a certain point where any higher caused an increase to occur in both the resistivity and Hall mobility.

### Refractive index

The refractive indices of all seven materials showed no significant change with chamber pressure. ZnSe, ZnO, and  $Y_2O_3$  showed a slight increased initially before reaching 1.0 x  $10^{-4}$  Torr, but the values than saturated for higher pressure values.

### Absorption coefficient

The amount of light absorption remains relatively the same for  $Si_3N_4$  and  $SiO_2$ . ZnSe, ZnO, and  $Y_2O_3$  steadily increased in value with higher pressures. While also exhibiting an increase,  $TiO_2$  and PbTe showed a much larger difference.

### Bandgap

The bandgap of the materials increased for higher pressures, and this can be explained due to the difference in crystal structure of the material. The higher pressure leads to more amorphous films and therefore a greater mismatch in the growth planes.

# 5.3.4 High Power Neutralizer Current

The role of the HPN is to inject electrons into the beam path. This serves as three purposes. The first is to adjust the electron to beam ratio, which will neutralize the charge of the plasma. This adjustment can be made by changing the HPN current(175). This can result in different properties of the materials with changes in the conductivity, film stress, and refractive index. The second role of the HPN is to prevent deflections from the target and target charging. Target charging can become an issue because it can modify the stoichiometry of the films. In general, a negatively charged target will deposit films that have more tensile stress, and positively charged targets will deposit films with compressive stress. Also, a positively charged target can lead to films with higher resistance and an induced electrical field which will repel the ions to cause a more divergent beam(185). Proper control of the HPN parameters can be used to prevent the accumulation of charges on the target. The advantage to this is the stability of the ion beam. This and the flux of electrons reaching the target are controlled by the bias voltage of the HPN(185).

# CHAPTER 6

# Material Selection and Refinement

As discussed in Section 2.4, the IBSD system is such a powerful technique because of its flexibility in achieving a wide range of material characteristics tunable for different applications. However, this also makes it a very complex system there are several trade-offs between material properties. This explains the necessity of the relationships and spatial parameter mapping of Chapter 5. This subsection is an overview of the characterization tools needed in order to achieve specific material properties, as given in Tables 6.1 and 6.2.

# 6.1 Utilization of Deposition Parameters

This section discusses how each targeted objective can be achieved with utilization of the appropriate material parameters.

Property	Characterization Tools	Comments
Low stress and strain	• XRD	Especially important when working with long wavelengths when the structures can become quite thick and the high amount of stress or strain can lead to peeling, cracking, and/or buckling of the films
Thermally stable	• XRD	While the refractive index of the material will most likely shift for different temperatures, it is desirable to prevent other properties, such as crystallographic orientation, from changing
No interfacial mixing	• SEM	The energy of the ions can be quite high on the order of 1 keV. The films must have strong atomic bonding and robustness to be able to withstand the high energy bombardment to prevent problems.
Smooth surface	<ul><li> AFM</li><li> Optical microscope</li></ul>	Needed to avoid light scattering or unwanted deflections that can happen from bumps, hills, and voids
Good adherence	<ul><li>Scratch test</li><li>SEM microscope</li></ul>	Delaminating of the film from the semiconductor can lead to unwanted changes in the structural, electrical, and optical properties
Controllable adherence	• SEM	Accurate film thickness is desired in the order to achieve the desired phase changes
Uniform and homogeneous	<ul><li>SEM</li><li>Ellipsometry</li></ul>	Consistent material properties, both laterally and longitudinally desired
Conformal coverage	<ul><li>SEM</li><li>Ellipsometry</li></ul>	Needed for insulation or enhancement of non- planar features
Low surface oxidation	• SEM • FTIR	Prevents leakage current, non-characteristic absorption bands, and change in refractive index
Easily etched	<ul><li>SEM</li><li>Chemical acid etching</li></ul>	Required for openings such as metal contacts

Table 6.1: Summary of the necessary characterization tools for achieving the targeted material properties and a description of the importance of each property

=	Property	Characterization Tools	Comments
-	Minimal material defects	• Chemical acid etching	Reduces the amount of absorption and leakage
	Minimal interface defects	• PL • C-V	Reduces the leakage current due to surface states
	High film density	• Chemical acid etching	Avoids unwanted problems that can lead to inoperability such as dielectric breakdown. In addition, a high film density can help to protect the material and surface.
	Highly insulating	<ul><li> Hall measurements</li><li> C-V</li></ul>	Avoids shorting or unintentional creation of conduction paths.
	High breakdown strength	• Hall measurements	Avoids problems with complete failure of the films
	Appropriate refractive index	<ul><li>FTIR</li><li>Ellipsometer</li></ul>	Important to achieve the desired optical performance
	Low absorption coefficient	<ul><li>FTIR</li><li>Ellipsometer</li></ul>	Prevent unwanted light loss, which can be significant problem for thick structures

Table 6.2: Summary of the necessary characterization tools for achieving the targeted material properties and a description of the importance of each property

# 6.1.1 Packing Density

Higher film density is desirable for many applications. It allows for more controlled etching, better mechanical strength, smoother surfaces, lower leakage current values, and lower absorption. Section 7.7.2 discusses challenges with dielectric breakdown strengths, found related to the packing density.

The way to achieve a densely packed film is to arrange the particles with as little spacing between grains as possible with an absence of voids in the film. The higher density is achieved by modifying certain processes such as the energy of the particle before it adsorbs, mobility of the particle along the surface, and controlled positioning of the particles. The first important factor for high density is energy. Extra energy will provide the adatoms the ability to mobilize along the surface. Whether the energy is supplied thermally or not, hopping to sites with lowest energy will help to fill in voids and vacancies(99). The extra energy can be supplied by adjusting the RF power(149), substrate temperature, beam current, or beam voltage. The accelerator voltage or chamber pressure(189) can also influence the energy, but in an indirect way by modifying the energy of the particles with fewer collisions and higher acceleration rates.

Another factor is the deposition rate. Higher densities are typically achieved with lower deposition rates. A lower deposition rate allows the particles to have a longer amount of time to mobilize along the surface. If the time is too short, this can lead to an incoming particle landing on the surface and trapping the particle(24) before it gets a chance to fill a void. While higher RF powers, high substrate temperatures, higher beam current, lower chamber pressure, and higher accelerator voltage are ways to achieve denser films, using values that are past a certain threshold can undo the benefits because of effects such as resputtering. So, this should be taken into consideration.

## 6.1.2 Film Stress

There are three contributions to the overall stress of a material: extrinsic, stress due to thermal expansion and intrinsic stress. Extrinsic stress is induced when the material interacts with the environment. One example is the adsorption of water or hydrogen. Stress due to thermal expansion occurs when a layer has a mismatch in its thermal expansion coefficient compared to either another layer or the substrate. Finally, intrinsic stress typically forms during the deposition and causes issues such as buckling. One example why it is important to consider is because it may affect the adhesion of the material to the substrate. This section provides a discussion on the intrinsic stress and how to control it.

Intrinsic stress is due to crystallographic flaws that accumulate during the deposition process. The amount of intrinsic stress for a given material varies, but in general, it will be higher when the deposition of materials with high melting point occurs at low substrate temperatures. The intrinsic stress consists of two different types: tensile and compressive. These types of stress are important because they can become the major factor of mechanical failure of the films. Consideration of tensile stress is necessary for proper adhesion of the film to the substrate, and compressive stress for thick structures. The IBSD system
typically deposits films more compressively stressed due to the bombardment of the high energy ions. One of the advantages of IBSD is the high density films produced, but this also leads to higher compressive stress whereas porous materials tend to be more tensile.

There are many different parameters on the IBSD system that can be worked with to adjust the stress from being less tensile or less compressive. For a film with high tensile stress, high substrate temperatures during the deposition process can be a major factor causing this. The ion flux can also have an effect, but its influence depends on the actual temperature value. Higher temperatures will cause lower momentum transfer and higher chances of a chemical reaction, which leads to higher tensile stress. The higher temperatures will lead to adsorption of gases from the grain boundary to the columns of the microstructure. As a result, the surface free energy will increase and the grains will have a more vigorous interaction(99). The pressure during the deposition has a similar effect, where high pressures will lead to films that are more tensile. The high pressure will cause shorter mean free path lengths, so the particles experience more collisions. This causes both the ions and target atoms to bombard the substrate with less momentum and at more oblique angles. The microstructure must also be considered because one that consists of voids and grain boundaries tend to have tensile stress due to the attractive force exerted by the grains.

If the objective is to deposit a sample with less compressive stress, then the energy of the atoms and the state of the gases need to be considered. Compressive stress is influenced by sputtering of atoms ejected with higher energy (172) and its resulting recoil implantation (149). There are many parameters that can be used to control this, such as RF power of the primary deposition source, chamber pressure(178), flux of the argon ions(14), and substrate-to-target angle(183). Compressive stress is greatly influenced by atomic peening, which occurs when argon atoms reflect off the target surface, impinge the substrate at close to normal incidence, and imbed itself into the film due to the high momentum transfer. In the atomic peening phase, the stress in a material will abruptly change from tensile to compressive. The potential difference across the target and substrate can lead to higher or lower energies of these ions at the substrate surface. If the substrate is more negatively biased, then the films tend to be compressive. The ion bombardment plays such a significant role with the formation of compressive stress because of changes in microstructure from the momentum transfer involved. The stress is due to the microstructure of the sample, and this can become an issue with the incorporation of impurities like oxygen(14) and trapping of gases within the film. The deposition parameters can greatly influence the amount of compressive stress; however some materials will be more susceptible than others. In general, deposition using a sputtering gas with low atomic mass and target material with high atomic mass will lead to more compressive stress. Finally, another way to reduce compressive stress is with post-deposition annealing. Annealing of the sample leads to higher atomic mobility, so atoms will move to favored sites such as voids, grain boundaries, and interstitials causing relaxation.

In summary, the issues of stress are largely dependent on the growth conditions and microstructure of the material. This can be illustrated in Figure 6.1. Higher momentum transfer from conditions such as low substrate-to-target angle, high RF power, and high sputtering pressures will lead to high compressive stress. With these conditions, the bombardment of the substrate occurs at an angle normal or near-normal incidence. As a result, ions or atoms can become imbedded into the films and the grains will exhibit a repulsive force against each other. An added step to reduce the repulsive force is postdeposition annealing which can drive out the trapped gas particles. The material outcome tends to be films that are smooth, densely packed, and have good adhesion. On the other hand, films that have tensile stress tend to be rough, porous, and have poor adhesion.



Figure 6.1: Bombardment of ions and target atoms at angles normal to the substrate leads to films more compressively stressed and at oblique angles lead to more tensile stressed films. The illustration shows how higher compressive stress is induced when gaseous atoms become trapped in-between grains

### 6.1.3 Amorphous and Polycrystalline Films

Achieving crystalline films from IBSD is difficult and rare, but it can reliably produce both amorphous and polycrystalline films depending on the growth conditions. Since the work here benefits from both, this section will discuss how materials can be deposited to ensure the appropriate crystalline nature is achieved. The basic idea to polycrystalline films is that the atoms need enough time and energy to mobilize and orient along a specific plane. This is desirable for almost applications discussed in Chapter 8. In particular, it is desirable for electrical passivation to have polycrystalline films so that the atoms at the surface can satisfy the dangling bonds. If the material were amorphous, the arrangement would become random and the probability of satisfying the bonds is low. On the other hand, amorphous films are desirable for applications such as optical coatings as discussed in Chapter 7. The reason why amorphous films are desirable is because the film absorption will be low from minimal amount of light trapping and scattering.

Amorphous materials are achieved when the deposition process hinders the grain growth. This can occur in many different situations, such as high partial pressures(182). The reason why this has an effect is because the high pressure leads to shorter mean free path length. This leads to a higher frequency of collisions, so the atoms tend to bombard the substrate from random directions and angles. This also means that the substrateto-target angle can be adjusted for the same reasons. Another factor with amorphous materials is the energy of the atoms. Atoms with high energies will have higher mobilities that allow them to rearrange and orient along the correct plane to form a good crystal, so low energy atoms are desirable. Sources of energy include the substrate temperature and pressure. Parameters such as lower RF power value will help to achieve more amorphous films.

To achieve more crystalline materials, the first thing that is very important is the substrate quality. A substrate that has good crystalline properties will promote good grain growth on the first initial layer, and the effect can propagate as the layers are deposited. The important factors that aid better crystalline properties are mainly energy and time. The kinetic energy of the atoms is important because the higher energy will allow the atoms to move around the surface. Time is important because the atom needs to be able to reach the lowest surface energy before it is trapped by other atoms depositing on the surface. So the energy of the atoms can be promoted by using high RF powers or high substrate temperatures. Additionally, low sputtering pressures and small target-tosubstrate distance can help because both will reduce the frequency of collisions. The result of this is high energy atoms that reach the substrate in a controlled manner. However, caution must be taken because the controlled manner can become disturbed by RF powers that are too high or an increase in the gas bombardment. The higher gas bombardment, adjusted with parameters such as gas flow rates, will degrade the crystalline property due to the surface damage that is created. However, there are a few exceptions, as demonstrated in Ref. (139) where a slight amount of oxygen was needed to promote polycrystalline growth. So, there is a tradeoff between substrate temperatures, chamber pressure, RF power, and gas flows. Finally, a slow deposition rate is desired for reasons discussed earlier. This is especially true for reactive sputtering where the arrival rate of the atoms not only affects the crystalline quality but also has a large affect on the stoichiometry. After the deposition process has been completed, if permitted, annealing can be used for improved crystalline properties. The annealing gives the atoms a chance to rearrange into the crystal pattern.

While annealing is expected to help improve the crystalline quality of a material in most cases, this should not always be expected. The XRD scan of a polycrystalline ZnO sample deposited by IBSD on  $Al_2O_3$  is shown in Figure 6.2. A peak is exhibited around 17° due to either the (0002) or (1011) plane. However, no change in the peak's intensity

and no further peaks arose when the samples where annealed up to 1000 °C.



Figure 6.2: XRD measurements of ZnO

### 6.1.4 Interfacial Defect Density

A high density of interface defects is unwanted because it can lead to poor device performance. While high energies for the ions and atoms are useful in achieving dense films, it is disadvantageous because it can cause surface damage or the creation of interface defects. For the same reasons, increasing gas flux will also lead to more surface states. In other words, the deposition should occur at low RF powers, low sputtering pressures, low discharge voltage(190), and low gas flow rates in order to avoid this issue. Surface damage can come from any of those factors, and additionally, it can occur when the potential difference between the target and substrate is such that the negative ions experience a greater amount of acceleration. To avoid this, the potential difference should be kept the same to eliminate the energetic bombardment(11). The properties of the negative ions are important for this objective because they have been found to be one of the major contributing factors. Not only are the traps at the interface due to surface damage, but also to differences in work function, differences in lattice mismatch, and the presence of impurities(176) so this should be taken into consideration.

There are two more ways to reduce the density of interface states. The first is the utilization of the native oxide layer. The oxide layer can act as a physical protectant from the high energy ions. However, one disadvantage to this is that the native oxide layer can lead to interfacial instability and can be a source for charge trapping(92). The second action that can be taken is post-deposition annealing. Using a forming gas, the density of the traps located at the interface can be decreased(112).

### 6.1.5 Surface Charge and Flatband Voltage

The surface charge and flatband voltage of film is associated with the concentration of the carriers or interstitial atoms. The scattering of carriers leads to factors such as decreased carrier mobility and higher resistance. In addition to this, the surface charge and flatband voltage can be affected. The ability to tune the surface charge and flatband voltage allows for the capability of satisfying a wide range of objectives.

The main parameter used to influence the surface charge or flatband voltage is the ion assistance. It can be used to lead to higher positive fixed charge by using, for example, a higher oxygen gas flux. A plot demonstrating this is given in Figure 6.3. The flatband voltage can be varied from  $V_{FB} = -3.6$  to 7.2 V by merely adjusting the oxygen flow rates in the secondary assistance source. So, a higher flow rate will lead to a dielectric with more positive flatband voltage value. The charge can be located either in the dielectric itself or trapped within interface states(92). It should be noted that at certain frequencies, the trapping of charges can change, leading to an overall charge alteration of the material.



Figure 6.3: C-V curve of 5 different MIS structures with  $SiO_2$  deposited using different  $O_2$  gas flow rates in the secondary assistance source. A shift in flatband voltage is exhibited showing a that higher oxygen flow rates lead to a more negative fixed oxide charge.

#### 6.1.6 Refractive Index and Film Stoichiometry

The refractive index of a material is highly dependent on the stoichiometry and composition of a material. Often times, a precise refractive index is desired, especially for optical applications. However, not all refractive indices are available, so this section discusses how the deposition parameters can be used to achieve a deviation in the refractive index.

One of the major reasons why stoichiometric films have not been achieved when using the IBSD system is because of preferential sputtering. Preferential sputtering is the process of choosing preference an atom to be sputtered over another atom in a compound material. In general, preferential sputtering occurs for atoms with lower surface binding energy and/or lighter mass. As a result, the material will be deficient and the refractive index will adjust accordingly (8). There are three ways this can be resolved or alleviated. One way is with the utilization of a reactive gas in the secondary source. The reactive gas can be used to compensate for any losses that occur due to the preferential sputtering. This is demonstrated in Figure 6.4. The ideal refractive index of  $SiO_2$  is around n = 1.46, and the secondary source can be used to achieve values from n = 1.25 - 1.65. This is done by varying the composition of  $SiO_x$  from x = 1.3 to x = 3.3. The end result is a change in the transmittance, as shown in Figure 6.5. Second, control of the ion beam parameters can be used to adjust the amount of preferential sputtering making it insignificant. This can be done by using lower RF powers or lower sputtering pressures(149). Finally, the adjustment of both the RF power and pressure can change the type of particle that will reach the substrate. It has been observed by Ref. (191) that a sample exposed mainly

to ions has a different composition from a sample exposed mainly by neutrals even if the kinetic energy is the same.

Three more last methods can be used, but there is not as much control or variation compared to the parameters discussed earlier. The first is the adjustment of the sticking coefficient and oxidation rate. The sticking coefficient can be modified with parameters such as the substrate temperature. This could tailor the percentage of a certain atom that would stick to the substrate, given that the atom is present at the substrate surface(178). The densification can also be modified. In general, more densely packed materials will have a stoichiometry close to ideal, and a higher density of voids usually results in lowering of the refractive index. Finally, annealing can be used to improve stoichiometry(175) through enhanced diffusion, especially in the ambient of a forming gas.

### 6.1.7 Absorption Loss

The absorption loss is an important optical property for optoelectronic devices and optics. A higher absorption amounts to lower light intensity. Absorption that occurs within a material typically occurs due to either light scattering or light trapping. Light scattering occurs at the surface, where the roughness can deflect the light in an unwanted direction. This can be avoided by achieving smooth surface morphology. Light trapping occurs in between grains, where the spacing and voids can confine the light. This can be avoided by producing films that are dense and amorphous. Densification can be achieved with higher energy and angle of incidence of the incoming ions. Amorphous materials can be achieved by using high chamber pressures or low substrate temperatures (149) to prevent



Figure 6.4: Change in refractive index of  $SiO_2$  for different oxygen flow rates in the secondary source and its corresponding composition. A higher oxygen composition shows to coincide with a lower refractive index and vice versa

nucleation(178). The trade-off between choosing high substrate temperatures, RF powers, and beam voltages for higher energy to achieve dense films compared to low substrate temperatures, high substrate-to-target angles, and high sputtering pressure for random orientation to achieve amorphous materials can become challenging. Further details on how to achieve high packing density can be found in Section 6.1.1 and amorphous material in Section 6.1.3.



Figure 6.5: Range of attainable transmittance values of  $SiO_2$  samples with changes in oxygen flow rates in the secondary assistance ion source. A higher transmittance is observed with higher flow rates, but values too high will cause the transmittance value to go down. This is due to the higher flux of oxygen atoms hitting the substrate

## 6.2 Alternative Techniques

Two alternative techniques that can be used to modify the film properties are reactive sputtering and annealing. Both will be discussed in this section.

### 6.2.1 Reactive Sputtering

In addition to sputtering a target made of the compound material, another method is to use a metal target and inject a reactive gas into the chamber to form the material through what is known as reactive sputtering. Each of the two methods has its advantages and disadvantages, as will be discussed here.

Reactive sputtering has very rough surfaces, but high deposition rates and low absorption coefficients. Tuning of parameters is easier because this process is more sensitive to the modifications from objects such as the secondary electrons and recoiled ions(190). This results in the energy and momentum of the secondary electrons and recoil ions changing the formation of nucleation sites(192). The sensitivity may be adjusting for fine tuning, but can lead to issues such as reproducibility since reactive sputtering is a nonlinear process(189).

The major advantage to sputtering with a target made of compound material is that the stoichiometry and material properties can be similar to the target material itself, provided that factors such as nuclear collisions do not significantly alter the ideal deposition. There are a few factors that need to be considered with reactive sputtering. First, the partial pressure has a much more profound effect with reactive sputtering with the reactive gas molecules moving randomly within the chamber. Second, the flow rate of the reactive gas hitting the target is important. If the rate is too low, the sputtering will be metallic and the compound film will not form properly. Finally, the material quality will be different so the choice between sputtering with a metal target and a metal-oxide target should depend entirely on the application and objectives. Example characterization differences for TiO<sub>2</sub> deposited using reactive sputtering and comparison to non-reactive sputtering are given in Figures 6.6, 6.7, 6.8, and 6.9.



Figure 6.6: AFM scans of  $TiO_2$  deposited with and without reactive sputtering



Figure 6.7: FTIR measured transmittance curves of  $\text{TiO}_2$  deposited with and without reactive sputtering

### 6.2.2 Post-Deposition Annealing

Post-deposition annealing can be used for slight modification of the material properties, especially with the structural and mechanical characteristics. The annealing temperature is expected to decrease the thickness of the material with values due to mobilization, densification, and diffusion. Typically the crystalline quality and growth orientation changes



Figure 6.8: FTIR measured reflectance curves of  $\text{TiO}_2$  deposited with and without reactive sputtering



Figure 6.9: Absorption of  $TiO_2$  deposited with and without reactive sputtering

resulting in is typically larger grain sizes due to the coalescence and enhanced crystalline quality (193). An example is shown in Figure 6.10, where a more rough surface is observed

due to the coalescence of annealing  $Y_2O_3$  at 700 °C in  $N_2$  for 2 minutes. Other changes due to annealing include reduced film stress(194) from relaxation(195). Additionally, the density of defects can be lowered or the material can become stabilized through annealing, given the appropriate forming gas is chosen.

Another effect with annealing is change in electrical properties. Since the density and grain structure is changing, lower resistivity with annealing temperature can be expected(141). This is especially true when annealing in certain types of forming gases. One example is given in Ref. (196) who showed how the resistivity of TiAlN was higher for higher temperatures of annealing in  $O_2$ . In addition to resistivity, the leakage current can be lowered with annealing due to a lower surface defect concentration(141).

Finally, slight modifications in optical properties can be experienced. Enhanced diffusion or incorporation of an inert gas can lead to changes in refractive index and stoichiometry. Further the optical PL can make changes based on annealing temperature, time, and gas such as a change in bandgap such as shown in Figure 6.11.



Figure 6.10: SEM cross-section of  $Y_2O_3$  film annealed at 500 °C for 10 min in  $N_2$  gas, showing a change in the morphology and microstructure.



Figure 6.11: Plot of PL of ZnO film annealed at three different conditions

# **CHAPTER 7**

## **Optical Coatings**

This chapter applies the dielectric thin-films used in this work to applications of optical coatings. Section 7.1 provides background information and important parameters such as refractive index. HR coatings are presented in Section 7.3. Further, three different types of AR coatings are discussed in Sections 7.4, 7.5, and 7.6. Single band AR coatings are then discussed in Section 7.4. Finally, Section 7.7 provides solutions to the experimental challenges that were faced in designing the optical coatings.

## 7.1 Background

In order to properly design, simulate, and model the optical coatings, it is important to understand the behavior of the wave through the coating structure, within each layer and at each interface. This section provides a discussion on the important characteristics and the equations necessary for modeling.

#### 7.1.1 Wave Properties Through a Medium

As a light wave passes through a material, its properties and characteristics change depending on the properties of the material. The properties of the material influence both the electric and magnetic field, and can be described by the permittivity and permeability. Permittivity and permeability represent the same concept with the difference of permittivity being applicable to electricity and permeability is applicable to magnetism.

The permittivity  $\varepsilon_r$  relates a material's ability to permit an electric field to pass through it. It measures the amount of opposition the material has to an electric field force. A material with larger permittivity will experience less opposition and therefore have greater capacitance and charge. Similarly, the permeability  $\mu_r$  relates a material's ability to permit a magnetic field to pass through it. It measures the amount of opposition the material has to a magnetic field force. The permittivity and permeability is related to the refractive index as:

$$n = \sqrt{\varepsilon_r \mu_r} \tag{7.1}$$

Due to the opposition of both electric and magnetic field forces, the speed of light in the material will change and this can be described with the refractive index. It causes the phase velocity of an electromagnetic wave to become a fraction of the speed of light. The refractive index N is a unit-less complex number whose relationship is given by:

$$\frac{1}{v} = \frac{N}{c} = \frac{n}{c} - i\frac{k}{c} \tag{7.2}$$

where v is the phase velocity and c is the speed of light. The real and imaginary parts of the refractive index represent two different losses: speed and amplitude. The real part of the refractive index n is dependent on the type of medium and affects not only the velocity of the wave, but also the angular direction of travel.

The imaginary part of the refractive index k is called the extinction coefficient. It is a measure of how well a material can scatter and absorb an electromagnetic wave that passes through the material. If an electromagnetic wave passes through a material easily, then it has a low extinction coefficient. Directly related to the extinction coefficient is the absorption coefficient. The absorption coefficient accounts for light loss per unit length, so it is geometry independent typically expressed in units of  $cm^{-1}$ . The relationship between extinction coefficient and absorption coefficient is given by:

$$\alpha = \frac{4\pi fk}{c} = \frac{4\pi k}{\lambda} \tag{7.3}$$

where c is the speed of light, f is the frequency, and  $\lambda$  is the wavelength. The oscillation amplitude of the electromagnetic wave will decay as it travels through the material, and the loss of power due to this is based on the absorption coefficient and distance x traveled through the medium. The power can be stated as:

$$\frac{P(x)}{P(0)} = \frac{\sigma E^2(x)}{\sigma E^2(0)} = \exp(\frac{-4\pi f kx}{c}) = \exp(-\alpha x)$$
(7.4)

Then the power intensity at a distance x can be stated by using the Beer-Lambert Law:

$$P(x) = P_0 \exp^{-\alpha x} \tag{7.5}$$

In addition to the change in power intensity, the real and imaginary parts of the refractive index will influence the amount of phase change of a material. The phase change will differ depending on the distance the wave vector must travel within the medium. Thus, the phase change is dependent on the thickness of the film d and the angle of transmittance  $\theta_t$ 

$$\delta = \frac{2\pi}{\lambda} N d\cos\theta_t = \frac{2\pi}{\lambda} (n - ik) d\cos\theta_t = \delta^r - i\delta^i$$
(7.6)

The absorption coefficient is an important parameter because it quantifies a geometryindependent amount of the incident electromagnetic wave that is consumed. Absorption bands exist in the IR due to distortions in the molecular bonds(19)(20). Each material contains a unique "fingerprint" determined through its absorption curve. This absorption curve can be used in quantifying the properties of the sample, especially its crystallinity.

The main source of absorption in the IR is lattice absorption where an interactive coupling occurs between incident light and thermally-induced vibrations that cause a change in the electric dipole moment. Lattice absorption is caused by band-to-band and band-to-excitons in the semiconductor material. This is different from the near-IR and UV, which has losses mainly due to electronic absorption. The difference makes the development high-quality thin films for IR optical applications more difficult, especially at longer wavelengths where the energy of absorption is lower. Only a small amount of energy is needed to trigger vibrational and rotational states in the IR. Furthermore, the probability of overtone absorption is much higher in the IR. Overtone absorption is absorption that occurs at multiple integers of the original frequency.

Atoms in a compound are connected through chemical bonds and their vibrations cause the absorption of IR energy. A molecule with n atoms has 3n degrees of freedom. Six degrees of freedom are for translations and rotations of the molecule, leaving 3n-6 degrees of vibrational freedom. When incident light interacts with the atoms, chemical bonds can stretch, contract, or bend. The chemical bonds between atoms can be found analogous to springs, which involve stretching and bending. In general, more energy is required to stretch or compress a bond than to bend it. This is why stretching vibrations are more commonly found at higher frequencies or shorter wavelengths, and bending vibrations are more commonly found at lower frequencies or longer wavelengths. The intensity of the absorption is determined by the magnitude of change in the chemical bond and its actual strength, so double bonds have a much higher intensity absorption band because they are twice as strong as single bonds.

Not all molecular vibrations cause the absorption of light. In order for absorption to occur, there are three conditions that must be met: (1)the vibrations must cause a change in the state of the electric dipole moment, (2)there exists an interaction between the incident electric field and dipole moment, and (3)incident radiation has the same energy or frequency as the vibrations. In general, the greater the change in state of the electric dipole moment, the stronger the absorption. When absorption occurs, both energy and momentum must be conserved, so the energy and momentum are transferred from the incident radiation to energy being used for the molecular vibrations. The exact frequency that a vibration at occurs depends on the bond strength and mass of the atoms(197):

$$v = \frac{1}{2\pi} \sqrt{k(\frac{m_A + m_B}{m_A m_B})} \tag{7.7}$$

The bond strength is represented by k, not to be confused with the extinction coefficient. This value is similar to Hooke's spring constant, typical values range between 3 - 8 x  $10^5$  dynes-cm<sup>-1</sup> for single bonds.

There two types of vibrations are shown in Figure 7.1 and Figure 7.2. The two types of stretching vibrations are symmetric and asymmetric with a change in the distance between bonds. The four types of bending vibrations are rocking, scissoring, wagging, and twisting with changes in the angle between bonds.



Figure 7.1: Illustration of the changes in bond length for different types of stretching vibrations: symmetric and asymmetric

In addition to stretching and bonding of the bonds, absorption can be exacerbated by coupling between vibrations. Coupling occurs when two neighboring vibrating bonds share a common, central atom, and the largest amount of coupling occurs when two vibrational bonds have the same exact energy. Thus no coupling can occur when vibrating bonds are separated by two or more bonds. There are three types of coupling: coupling of two stretching bonds, coupling of two bending bonds, and coupling between stretching and bending bonds. However, if their energies are slightly different than this, the resultant band will become a superposition of the individual vibrations. So, the absorption bands will overlap or appear to be one band that has broadened.



Figure 7.2: Illustration of the changes in bond angles for different types of bending vibrations: rocking, scissoring, wagging, and twisting

### 7.1.2 Wave Properties at an Interface

As discussed in the previous section, the change in wave properties as it travels through a material is affected by the refractive index. Additionally, the wave properties will change when it intersects a boundary. This is illustrated in Figure 7.3. The light changes its traversal angle when traveling from a medium with refractive index N<sub>0</sub> incident upon another medium with a different refractive index of N<sub>1</sub>. This change in angle is stated in Snell's law as N<sub>0</sub> sin $\theta_i = N_1 \sin \theta_t$ . While  $\theta_t$  is affected by the change in refractive index at the interface, the angle of reflected light,  $\theta_r$  is not.

To determine the light intensity transmitted and reflected at the interface, the Fresnel coefficients can be used. For both types of polarized light, the transmission and reflection



Figure 7.3: Drawing illustrating the action of an electromagnetic wave at an interface with different refractive index. Portion of the light will reflect at the interface at an angle  $\theta_i = \theta_r$  and a portion of the light will transmit through the interface  $\theta_t$ 

coefficient are given as:

$$t_{1p} = \frac{E_{tp}}{E_{ip}} = \frac{2\sin\theta_t\cos\theta_r}{\sin(\theta_t + \theta_r)\cos(\theta_t - \theta_r)}$$
(7.8)

$$r_{1p} = \frac{E_{rp}}{E_{rp}} = \frac{2\tan(\theta_t - \theta_r)}{\tan(\theta_t + \theta_r)}$$
(7.9)

$$t_{1s} = \frac{E_{ts}}{E_{tp}} = \frac{2\sin\theta_t\cos\theta_r)}{\sin(\theta_t + \theta_r)}$$
(7.10)

$$r_{1s} = \frac{E_{rs}}{E_{rp}} = \frac{2\sin(\theta_t - \theta_r)}{\sin(\theta_t + \theta_r)}$$
(7.11)

The transmittance and reflectance can then be found by squaring the coefficients.

$$T = |t_{1p}|^2 = |t_{1s}|^2 = \frac{4(n_0 - ik_0)(n_1 - ik_1)}{[(n_0 - ik_0)(n_1 - ik_1)]^2}$$
(7.12)

$$R = |r_{1p}|^2 = |r_{1s}|^2 = \left(\frac{(n_0 - ik_0)(n_1 - ik_1)}{(n_0 - ik_0) + (n_1 - ik_1)}\right)^2$$
(7.13)

The Fresnel coefficients are very useful, but only for describing the light interaction

at a single interface. To understand the properties of the light after it has traveled through the material, the tangential components of the electric field and the tangential components of the magnetic field must remain continuous across each interface. The tangential component of the electric and magnetic field is summed into one resultant positive and negative wave approaching from each side:  $E = E^+ + E^-$  and  $H = H^+ - H^ = \eta E^+ - \eta E^-$ . For a given layer (n+1), the electric and magnetic fields can be expressed in relation to the electric and magnetic fields of the previous layer n:

$$E_{n+1} = E_{n+1}^{+} + E_{n+1}^{-} = E_n \left[ \frac{exp(i\delta) + exp(-i\delta)}{2} \right] + H_n \left[ \frac{exp(i\delta) + exp(-i\delta)}{2\eta} \right]$$
(7.14)

$$H_{n+1} = H_{n+1}^{+} + H_{n+1}^{-} = E_n \eta \left[\frac{exp(i\delta) + exp(-i\delta)}{2}\right] + H_n \left[\frac{exp(i\delta) + exp(-i\delta)}{2}\right]$$
(7.15)

Simplification leads to:

$$E_{n+1} = E_n \cos \delta_n + \frac{i \sin \delta_n}{\eta_n} H_n \tag{7.16}$$

$$H_{n+1} = i\eta_n E_n \sin \delta_n + H_n \cos \delta_n \tag{7.17}$$

These equations can then be rearranged into matrix form, which looks like:

$$\begin{bmatrix} B\\ C \end{bmatrix} = \begin{bmatrix} E_{n+1}\\ H_{n+1} \end{bmatrix} = \begin{bmatrix} \cos \delta_n & i \sin \delta_n / \eta_n \\ i \eta_n \sin \delta_n & \cos \delta_n \end{bmatrix} \begin{bmatrix} E_n\\ H_n \end{bmatrix}$$
(7.18)

From the characteristic matrix, the transmittance and reflectance can be found equal to:

$$T = \frac{4N_0 Re(N_s)}{(N_0 B + C)(N_0 B + C)^*}$$
(7.19)

$$R = \left(\frac{N_0 B - C}{N_0 B + C}\right) \left(\frac{N_0 B - C}{N_0 B + C}\right)^* \tag{7.20}$$

For a system with multiple layer, the coefficients can be expanded out to account for each one, but this can become quite cumbersome as the number of layers increases. An alternative to this is to represent each layer in the system as a single matrix, simplifying the calculations. To extend this to a system with more than one layer, the resultant matrix can be found by taking the matrix product of each layer in the same order as it appears.

$$\begin{bmatrix} B \\ C \end{bmatrix} = \{\prod_{r=1}^{q} \begin{bmatrix} \cos \delta_r & i \sin \delta_r / \eta_r \\ i \eta_r \sin \delta_r & \cos \delta_r \end{bmatrix} \} \begin{bmatrix} 1 \\ N_s \end{bmatrix}$$
(7.21)

### 7.2 Equivalence Layers

Obtaining an accurate refractive index value is very important, especially when requiring low reflectance or high transmittance values. However, the ability to achieve one specific refractive index value can be difficult or maybe even impossible. One way to overcome this is by transforming a given layer with an unrealizable refractive index and thickness with its equivalence. This can be done since a multi-layer structure can be abstractly viewed as one entity with an effective refractive index. At a given wavelength, the equivalence can be substituted to achieve the same optical spectra provided that the characteristic matrices are the same(198).

To find the three-layer equivalent, three materials with refractive index  $n_p$ ,  $n_q$ , and  $n_r$ must be chosen and all that remains to be solved is each layer thickness  $d_p$ ,  $d_p$ , and  $d_r$ . This can be done by setting their matrices equal to each other, and the phase thickness can then be found using the following equations:

$$\tan \delta_q = \frac{-B}{2A} \pm \sqrt{\left(\frac{B}{2A}\right)^2 - \frac{C}{A}} \tag{7.22}$$

$$\tan \delta_p = -\frac{\varepsilon + \beta q}{\alpha - \delta q} \tag{7.23}$$

$$\tan \delta_r = \frac{\alpha - Epq}{\alpha p + \beta q} \tag{7.24}$$

$$A = \beta E + \delta F \tag{7.25}$$

$$B = \varepsilon E - \alpha F - \alpha \delta + \beta \varepsilon \tag{7.26}$$

$$C = \alpha^2 + \varepsilon^2 \tag{7.27}$$

$$\alpha = M_{22} - M_{11} \tag{7.28}$$

$$\delta = \frac{n_1^2}{n_2} \left(\frac{M_{21}}{n_1^2} - M_{12}\right) \tag{7.29}$$

$$\varepsilon = n_1 \left(\frac{M_{21}}{n_1^2} - M_{12}\right) \tag{7.30}$$

$$E = \frac{n_1}{n_2} \left(\frac{M_{22}}{(n_1/n_2)^2} - M_{11}\right) \tag{7.31}$$

$$F = \frac{n_1^2}{n_2} \left(\frac{M_{21}}{n_1^2} - \frac{M_{12}}{(n_1/n_2)^2}\right)$$
(7.32)

## 7.3 High Reflection Coatings

With optoelectronic devices, a large amount of energy can exit out. This energy is typically at a complete loss for applications that only utilize one side for emission or detection. One solution to this is to use high-reflection coatings. They can be used to prevent unwanted light loss out of a given side or end of the device. There are two types of HR coating structures: metallic and dielectric stack. The choice of which structure to use is dependent on the application and resources available. The advantages, disadvantages, and design of the structures will be discussed in this section.

### 7.3.1 Metallic High Reflection Coatings

Metallic HR structure is typically used when the targeted objective is to achieve the highest reflectance value possible. One of the main advantages of metallic HR coatings is that it is very simple to develop and work with. The metallic HR coating structure can be designed by simply using a single layer of a metal with high refractive index. One readily available metal with high refractive index is gold. The appropriate thickness to choose for the metal layer depends on the wavelength and its refractive index difference. It must be thicker than needed for saturation of the reflection value.

In addition, the structure must also contain an insulating layer. The metal layer is most likely conductive, and can pose problems if there is a conduction path to the semiconductor. The choice of appropriate dielectric layer has only one requirement of not being electrically conductive. This can be done by choosing a material that is thick enough with a high resistance. Other factors such as dielectric breakdown strength should also be considered for maximum performance operation.

Finally, one last layer is required to act as an adhesion layer between the insulator and the metal. If the layer is absorbing, making the thickness as small as possible will lead to a negligible effect on the performance of the HR coatings. In this work, titanium was used. This is a good material for this case because the gold layer can be deposited right on top of it in the same system without exposing it to atmosphere.

### 7.3.2 Dielectric Stack High Reflection Coatings

Dielectric stack HR coatings are most useful in situations when a high reflectance less than 100% is needed. This structure is more flexible with achieving different reflectance values. They can also be used when the appropriate single-layer metal is not available for the metallic HR coating.

The dielectric stack can be designed by using two different materials: one with a low refractive index and the other with a high refractive index. The greater the difference in refractive indices between the two materials, the more flexibility there is. Once the materials are chosen, the number of layers must be chosen. The simplest way to design this is by using odd number of layers, each with a thickness equal to a quarter-wave. Section 7.4.1 discusses how a quarter-wave thickness can be determined. The sequence of layers deposited is such that the material with high refractive index is deposited for the even numbered layers.

Near 100% reflectance can be achieved provided that the outermost layers have a high refractive index value. The light beams will reflect at each interface with an equal phase. When all light beams reach the interface of the outermost layer, they will constructively interfere to achieve a high reflectance. One problem this may pose is that the quarterwave can lead to very thick layers but this can be overcome by careful selection of the phase change. Also, the thickness must be considered and good values to be chosen can be founding using the characteristic matrix from Eq. 7.21.

#### 7.3.3 Experimental Results for Infrared Lasers

For lasers, HR coatings are typically used on the rear facet to prevent light loss out of the back end. In this case, 100% reflectance is desired and a very high reflectance can be achieved when using a metallic HR coating. One example is an HR coating for a  $\lambda \sim 9 \ \mu m$  laser. The minimum gold thickness required for reflectance saturation at this wavelength was found to be 80 nm(199), as plotted in Figure 7.4. The structure consists of 176 nm Y<sub>2</sub>O<sub>3</sub>/15 nm Ti/85 nm Au; the SEM measured cross-section and FTIR measured reflectance provided in Figure 7.5.

One point to note is that the use of different insulating materials and different thicknesses for the HR coating was experimentally found to have a negligible effect on the results of the lasers provided that they are sufficiently insulating. This is because the overall length of the laser cavity is significantly longer than the thickness of the insulator.



Figure 7.4: Plot showing the percentage transmittance and reflectance for different thicknesses of gold in a metallic HR coating. This is based on the refractive index of gold at  $\lambda \sim 9 \ \mu m$ 

The absorption loss in the HR coating is given as:

$$\alpha_{HR} \approx \left[\frac{d}{L+d} - \frac{\lambda}{4\pi n(L+d)}\sin(\frac{4\pi nd}{\lambda})\right]$$
(7.33)

where  $\alpha_{ins}$  is the absorption loss of the insulator, d is the thickness of the insulator, L is the cavity length, and  $\lambda$  is the emission wavelength of the laser. To prove this, three different HR coating insulators were deposited on the same laser: Si<sub>3</sub>N<sub>4</sub> by PECVD, Y<sub>2</sub>O<sub>3</sub> by IBSD, and ZnSe by IBSD. If the three insulators exhibited different performance behaviors, it would be due either to the reflectivity change from the differences in refractive indices or a change in transmittance due to their absorption coefficients. At the laser wavelength, the



Figure 7.5: Measured reflectance of a metallic HR coating. Inset shows the structure viewed under SEM

refractive index values differ by no more than about 0.5, and the absorption coefficient values of the three films differ by no more than about  $\Delta \alpha = 1200 \text{ cm}^{-1}$ . As can be observed, the L-I curves of the three lasers are nearly identical, and this will be the case provided the absorbance is not significantly large. The curves are provided in Figure 7.6.

Figure 7.7 provides a comparison of the P-I-V curve of a laser with and without an HR coating deposited on the rear facet. The HR coating used was a metallic coating with near-100% reflectance. The result of this is nearly double the output power where  $P_{out}^{uncoated} = 782.4 \text{ mW}$  compared to  $P_{out}^{HRcoated} = 1485.1 \text{ mW}$ , and a 73% reduction in threshold current density.



Figure 7.6: P-I curve of three identical lasers with HR coating consisting of different insulators. The insulator thickness is significantly smaller than the cavity length of the laser, so the curves are nearly identical

In addition to rear facet coatings, sometimes an HR coating on the front facet can be used to customize the amount of light transmitted out of the laser where a lower transmittance is desired. One such case is to use front facet HR coatings to shift the threshold current density to lower values. The dielectric HR coating was designed for a  $\lambda \sim 3.8 \ \mu m$  laser, consisting of 420 nm PbTe and 110 nm Y<sub>2</sub>O<sub>3</sub>. This structure is different from the one given in Section 7.3.2 with modifications made to account for compressive stress and electrical isolation. The measured reflectance is provided in the plot of Figure 7.8, showing a reflectance value of R = 56%. The plot of the average power for different duty cycles for the laser with and without a dielectric stack coating on the front facet is given in Figure 7.9. Measurements were taken at 10% above threshold. Since the threshold



Figure 7.7: P-I-V curve of two idential lasers one with and one without HR coating on the rear facet. A large difference in the power and threshold current density can be observed due to the prevention of light loss out of the rear facet.

is lower in the laser with front coating, the amount of internal heating is lower and thus the average power is higher. Comparing the same laser with different front facet coatings, higher average powers at higher duty cycles were achieved with the coated sample. It may be desirable to achieve continuous-wave operation, and with a higher reflectance this should be achievable. Further, the influence of the dielectric HR coating will become more pronounced with longer cavity lengths. One point to note is that similar to the metallic HR coating, the dielectric stack should be isolated from the bottom contact. In this work, this was done by masking the bottom of the facet, especially necessary since the PbTe layer was relatively thick.



Figure 7.8: Measured reflectance of a dielectric stack HR coating with reflectance near 60% at  $\lambda \sim 3.8 \ \mu\text{m}$ . The inset shows the structure measured under SEM.

## 7.4 Single Band Anti-Reflection Coatings

One limitation with the semiconductor devices is that the refractive index between air and the device leads to a restricted amount of light to exit out or transmit into the device. One solution to this problem is to use an AR coating to increase the amount of light input or output.

#### 7.4.1 Background

The objective for achieving zero percent AR coatings can be met with optical impedance matching. By making the output impedance equal to the input impedance, the power


Figure 7.9: Measured average power vs. duty cycle for a 3.8  $\mu$ m laser, with front facet coatings one without and the other coated with a dielectric HR stack. The laser with the dielectric HR front coating shows a higher average power due to the lower amount of induced heating. Continuous-wave operation is expected if a higher reflectance value is to be used.

transfer will be maximized. A closer match in impedance between the two media will lead to more light refracting through the boundary.

Matching the optical impedances can be done by satisfying two conditions: one for maximum amplitude and the other for constructive interference. The first criterion is to make the light vector reflected from the lower boundary equal to the light vector reflected from the upper boundary. This can be done by setting the ratio of the refractive indices at each boundary equal to each other. From Figure 7.10, the ratio of the refractive index at the upper boundary is  $n_0/n_1$ , and the ratio of the refractive index at the lower boundary is  $n_1/n_s$ . Setting these two equal, the refractive index of the AR coating must be:

$$n_{AR} = \sqrt{n_0 n_s} \tag{7.34}$$

The second criterion to be met is achieving complete constructive interference, which means that the light vector is 180° out of phase. Assuming normal incidence, this means that the light vector at the lower boundary must be 90° out of phase. For a targeted wavelength  $\lambda$ , a 90° phase difference can be achieved by using a thickness equal to a quarter-wave given by:

$$n_1 d_1 = m\lambda/4 \tag{7.35}$$

where m is any positive integer. At odd integrals of  $\lambda$ , the reflectance is at a maximum value, and at even integrals, the reflectance is at a minimum value.



Figure 7.10: Drawing of a single layer and double layer AR coating illustrating the order of the layers

#### 7.4.2 Single Layer Anti-Reflection Coatings

The two criteria mentioned in the previous section can be used to achieve an objective of lowest reflectance. However, slight modifications must be made if the objective is highest transmittance instead of lowest reflectance since the criteria does not account for absorption. The reason why this is suitable is because the absorption will reduce the transmittance and have an insignificant effect on the minimum achievable reflectance value. To achieve the objective of highest transmittance, the real part of the refractive index is made higher to account for phase changes. With this adjustment, the phase change will reduce the loss in transmittance, but at the cost of higher reflectance due to the larger difference in refractive indices. To choose the appropriate material, each one was deposited with a thickness to a quarter-wave. The optimization of the deposition parameters were done with the objective of lowest amount of absorption.

For a targeted wavelength of  $\lambda \sim 5 \ \mu m$ , the FTIR curves were measured as shown Figure 7.11. A few observations can be made from the curves. The reflectance values vary with wavelength due to dispersion of the refractive indices. This would mean that the layer thickness would have to be adjusted for different targeted wavelengths. Also, it is determined that a higher residual reflectance than desired is usually achieved. This is because the materials used did not have the exact targeted refractive index, and further the absorption coefficient values were non-zero.

Due to the limitations, the single layer AR coating structure is found insufficient for obtaining 0% reflectance due to the inflexibility and fewer number of adjustable param-



Figure 7.11: FTIR measured curves of single-layer AR coatings deposited with quarterwave thickness. Since the six materials do not have a refractive index equal to the targeted refractive index, a non-100% transmittance value was achieved.

eters. A resolution to this problem is to use two layers, as will be discussed in the next section.

### 7.4.3 Double Layer Anti-Reflection Coatings

To overcome problems with the single layer AR coatings described in the previous section, a double layer structure can be used. The double layer is essentially an extension to the single layer with preservation of the targeted refractive index and optical thickness value. In order to develop the double layer structure, two materials are first chosen: one with a refractive index value lower than the targeted and the other with a refractive index higher. The order and thickness of the layers is then determined by ensuring optical impedance matching, which leads to three different expressions:

$$n_2^2 - n_0 n_s \tag{7.36}$$

$$n_1^2 n_s - n_0 n_2^2 \tag{7.37}$$

$$n_0 n_s - n_1^2 \tag{7.38}$$

A valid solution exists if either (a)all three expressions are positive or (b)any two expressions are negative and the third is positive. The two requirements can be visualized using a Schuster diagram(200). There are two types of Schuster diagrams: one for quarter-wave thick layers and another for non-quarter wave thick layers. There are advantages(185) and disadvantages to using either diagram. The advantage to using quarter-wave thick layers is that the thickness of each layer can easily be determined. While quarter-wave thick layers are simpler, using non-quarter-wave thick layers provides more flexibility due to a higher number of available combinations. This is because the non-quarter-wave thick layers does not have to follow a specific order, while the quarter-wave thick layers must be have  $n_0 < n_1 < n_2 < n_s$  be true. Further, the choice also depends on the objective. If the objective is lowest reflectance, any combination of two materials with the right thickness will work. If the objective is highest transmittance, then the best choice of the different combinations is dependent on the absorption coefficient.

An example Schuster diagram for a quarter-wave thick double-layer structure on top of ING substrate is given in Figure 7.12. The valid double-layer structure can be found with the intersection of the refractive indices of the layers in the shaded region. Dark black lines border the shaded region and these lines are represented by the equations:  $n_1 = n_2$  and  $n_1 = (n_0/n_m)^{1/2}n_2$ . If these materials did not have film absorption, then any one of the combinations of quarter-wave double-layer AR coatings could be chosen. However, since absorption is almost always present, then each of the combinations must be experimentally tested to determine the best structure.



Figure 7.12: Schuster diagram for double layer AR structures showing possible combinations using quarter-wave layer thicknesses. The advantage of using this diagram over the one shown in Figure 7.13 is simplicity in determining the thickness value

The non-quarter-wave-thick Schuster diagram is shown in Figure 7.13. Similarly, the valid combinations are given by the shaded region with surrounding black lines, and the equations of these lines are  $n_2 = (n_0 n_s)^{1/2}$ ,  $n_1 = (n_0 n_s)^{1/2}$ , and  $n_1 = (n_0 n_s)^{1/2} n_2$ . The thickness of the layers can be determined using the characteristic matrix theory presented

in Section 7.1.2



Figure 7.13: Schuster diagram for double layer AR structures showing possible combinations using non-quarter wave thickness. The advantage of using this diagram over the quarter-wave thick diagram is the large number of possible combinations.

While the issue of achieving the targeted refractive index was resolved, there still exists the problem of layer thickness values being large. The thick layers are prone to peeling or cracking due to film stress or strain, so mechanical failure may result. To overcome this issue, multiple layers are used as discussed in the next section.

### 7.4.4 Multi-Layer Anti-Reflection Coatings

Multi-layer AR coatings can be used as a solution to structural and mechanical problems. The most common way of developing an AR coating is by simply use quarter-wave thick layers with a layering sequence that ensures the ratios of the refractive indices at each boundary are equal  $(n_0/n_1 = n_1/n_2 = n_q/n_s)$ . There are two major disadvantages to this approach. The first is that the layers are still very thick, and second, the thickness of the layers is only accurate if the films are non-absorbing. Since it is very difficult, if not impossible, to deposit and find non-absorbing dielectric thin-film materials, then this design does not typically result in R = 0%.

An efficient design for a multi-layer structure is done by using the same two materials used in the double-layer structure, preserving its effective refractive index and total optical thickness. A certain number of stacks are chosen with alternating between materials in the same order as the double layer structure. The physical thickness of each layer is equal to the physical thickness of that material from the double layer divided by the number of stacks. The reason why this can be done is because the effective refractive index is not changed.

The number of stacks should be chosen with the highest number possible without limitations to the accuracy of the thickness of the films, since the layers become thinner with a larger number of stacks. The advantage to using a large number of stacks is that as the number of layers increases, the minimum reflectance point begins to decrease. As a result, the reflectance band will begin to narrow in wavelength span. This can be explained due to the optical impedance mismatch. The wavelength of light in the first medium can be related to the wavelength of light in the second medium by using the ratio of optical impedances:  $k_1 = k_2(Z_1/Z_2)$  where k is the wavenumber. If the impedance at each boundary is not exactly matched, as is the case with fewer and fewer number of layers, then this leads to different angles of reflection. This leads to broadening of the reflectance band, but at the same time the mismatch is greater and therefore will lead to a higher minimum reflectance. For single band AR coatings, the width of the reflectance band is typically larger than the span of wavelengths for device operation.

The substitution using this methodology is allowable because the optical properties of any structure will remain the same as long as the optical admittances are either multiplied by a constant factor or replaced by their reciprocals. The only possible exception is when interfacial mixing occurs because the poor interface quality can change the optical properties.

#### 7.4.5 Experimental Design and Procedure

The procedure used for developing the appropriate single band AR coating structure is given in this section using the same process discussed earlier. In this example, the targeted objective was a single band AR coating for a  $\lambda \sim 9.4 \ \mu m$  laser. The top four double-layer structures from the Schuster diagram were simulated, and the results are given in Figure 7.14. Each structure was deposited and characterized. The results are given in Figures 7.15, 7.16, 7.17, and 7.18 with a summary provided in Tables 7.1 and 7.2.

From these characterization results, the top structures were chosen and extended into multiple layers. Double-layer #1 was not chosen because its transmittance was very low. Double-layer #3 had issues with peeling even though this structure was predicted to have the second highest transmittance. The issues were due to properties of the ZnSe material. It is very soft, which makes it easily removable and/or damaged by the highly-energetic ions. Further, another problem is that special conditions are required in order to achieve proper adhesion to the substrate. This leaves the choice to be either double-layer #2 or double-layer #4.



Figure 7.14: Top four double-layer structures determined by simulation for a  $\lambda \sim 9.4 \ \mu m$  laser



Figure 7.15: AFM scans of the four single band anti-reflection coatings

Double layer #2 and double layer #4 were extended into multilayers of a 6-layer PbTe/ZnO structure and an 8-layer ZnSe/ZnO structure, both deposited on ING substrates, as shown in Figure 7.19. The appropriate thickness in the 6-layer PbTe/ZnO

Summary	of	Characterization	Results
-/			

### Double layer #1

AFM Small grain sizes. Measured RMS roughness of 1.829 nm

- SEM Very thick  $SiO_2$  layer has formed between the  $Y_2O_3$  layer and the silicon substrate due to the large amount of gaseous oxygen atoms used in the secondary assistance source. A reduced amount of oxygen flow during the initial stages of growth is effective in minimizing the thickness of the natively formed  $SiO_2$ . A poor interface is seen due to interfacial mixing, where the parameters of the secondary assistance source for ZnSe have caused initial damage of the  $Y_2O_3$  layer underneath. This poor interface makes it very difficult to determine the exact layer thicknesses.
- FTIR The maximum transmittance and minimum reflectance occurs around 4.8  $\mu$ m, which is an indication that the thickness values are incorrect. However, adjusting the thickness should shift the location in maximum transmittance and minimum reflectance. Low transmittance values due to high absorption in the film.

#### Double layer #2

- AFM High RMS roughness of 5.220 nm due to the large spikes and hills seen on the surface. The large spikes and hills can be attributed due to the growth of PbTe on top of ZnO because no spikes or hills were observed for the deposition of the first layer of ZnO.
- SEM Not observed under SEM due to the presence of spikes on the surface.
- FTIR One of two of the highest transmittance. The reflectance values less than 3%
- AFM Scan not provided, instead picture of top surface view from optical microscope is provided. The peeling issues can be attributed due to the adhesion of the two materials and also due to the rough, damage surface that the ZnO is deposited on top of.

Table 7.1: Summary of the characterization results from deposition of double-layer #1 and double-layer #2 structures.

	Summary of Characterization Results			
Double laver #3				
AFM	Scan not provided, instead picture of top surface view from optical microscope is provided. The peeling issues can be attributed due to the adhesion of the two materials and also due to the rough, damage surface that the ZnO is deposited on top of.			
SEM	Interfacial mixing observed. The ZnSe layer after the deposition of ZnO layer on top of it is shown to be nearly half the thickness of the original ZnSe layer. The bombardment of the secondary assistance directed towards the sample results in a resputtering of the ZnSe film, and therefore half of the film thickness has become removed.			
FTIR	Low transmittance values due to high absorption in the film. Reflectance value less than $3\%$			
Double laver #4				
AFM	Measured RMS roughness of 2.363. Grains look good, except there are voids present.			
SEM	The interface between the two layers looks good as observed, except film stress in the thick ZnO layer is observed.			
FTIR	One of two of the highest transmittance. The reflectance values for all structures were less than 3%.			

Table 7.2: Summary of the characterization results from deposition of double-layer #3 and double-layer #4 structures.



Figure 7.16: Cross-sectional view of double layer structures #1, #2, and #4



Figure 7.17: Plot of the transmittance of all four double layer structures for single band AR Coating

structure was 20 nm for the PbTe layers and 310 nm for the ZnO layers. The design was capped at six layers because of concern with its accuracy for values less than 10 nm. The structure was deposited on substrate, and the characterization results are given in Figures 7.20 and 7.21. The AFM scan of the PbTe/ZnO multilayer still showed small bumps on



Figure 7.18: Plot of the reflectance of all four double layer structures for single band AR Coating

the surface. However, the frequency and intensity is not as significant as in the case of the double-layer structure. The small hills on the surface are spaced around 0.5 - 1  $\mu$ m apart, which is most likely an insignificant source of light scattering. The SEM picture still shows hard-to-distinguish interfaces between the PbTe and ZnO layers.

The second structure was an 8-layer ZnSe/ZnO structure with a simulated thickness of 60 nm for ZnSe and 218 nm for ZnO. Its double layer structure had more desirable optical properties than the PbTe/ZnO double layer structure. However, when extending the ZnSe/ZnO double layer to eight layers, a problem was encountered. The high power and high ion energy used for the deposition of ZnO caused damage to the ZnSe material. This damage occurred any time when depositing on top of ZnSe. This problem was the



Figure 7.19: Extension of double-layer #2 and double-layer # into multilayers. A second structure was designed for the multilayer coating structure consisting of ZnO/ZnSe due to structural issues of interfacial mixing and peeling.



Figure 7.20: AFM scans of single band AR coating multi-layer structures

same as seen for double layer #3. To overcome the problem of interfacial mixing and damage, a lower power in the secondary-assistance ion-source can be used, either for the entire duration of the deposition or during the initial few nanometers of growth. Another solution would be to only use the primary ion source and not the secondary source. However, this can lead to porous materials with low dielectric breakdown strengths. Since lowering the power of the ion-source for the entire duration of the deposition would result in completely different and more absorbing film properties, as shown in Section 5.1.6, the decision was made to ramp the power. When depositing the ZnO layer, the power



Figure 7.21: SEM of single band AR coating multi-layer structures

of the secondary ion source must be small until a thick enough ZnO layer is grown to protect the ZnSe layer. This ramping caused different properties from the non-ramped ZnO layers, and therefore must be represented as a separate material which is considered a buffer layer. With this change, the structure had to be modeled as an 11-layer structure with three different materials: ZnO, ZnSe, and ZnO buffer layer. The ramp conditions and time in order to achieve a thick enough ZnO buffer layer is given in Table 7.3. The 11-layer ZnSe/ZnO structure exhibited a smoother surface with reduced RMS roughness and no obvious damage was viewed under optical microscope. The smoother surface and smaller grain size can be attributed due to the smoothing of the ZnSe layer with the addition of the ZnO buffer layer. A contrast in colors of the buffer layers observed under SEM is due to the different composition compared to the ZnO without any changes in parameters.

The transmittance and reflectance spectra of the two multilayer AR coating structures are given in Figure 7.22 and 7.23. The reflectance values for both structures are

Time	Power[W]
30:00	214
5:00	245
5:00	283
1:00	314
1:00	345
1:00	387
0:30	405
0:30	488
0:30	533
0:30	613

Table 7.3: Deposition parameters and time for the secondary ion source used to deposit ZnO buffer layers

similar and reach low values around 1%. However, the transmittance curves are very different, especially in the wavelength range of 7 - 12  $\mu$ m, where up to 20% difference is observed. The reason is because the ZnO buffer layers used in the 11-layer structure led to a larger amount of absorption. This relationship between absorption and RF power was demonstrated in Section 5.2.1.

Due to the low absorption, the 6-layer PbTe/ZnO was chosen. However, a slight modification had to be made with the structure and this is because the minimum reflectance occurred at a shorter wavelength. The minimum reflectance was shifted by slightly increasing the layer thicknesses both by an equal percentage. Further, the maximum transmittance was lower than desired, so the total film absorption was effectively decreased by using thinner PbTe layer and thicker ZnO layers. Before the adjustments, the ratio of thicknesses of PbTe:ZnO was 2:31 with a total thickness of 990 nm. After the adjustments, the ratio was 2:69 with a total thickness of 1065 nm.



Figure 7.22: Comparison of transmittance of the single-band multilayer AR coatings



Figure 7.23: Comparison of FTIR reflectance of the single-band multilayer AR coatings

Figure 7.24 shows the cross-section of the structure observed using SEM. The final measured thickness of the layers were (347.1/10.8/349.2/9.8/347.5/10.5) in nanometers. The FITR measured transmittance and reflectance curves are provided in Figure 7.25, represented as solid lines in the figure. The theoretically simulated curves are also provided in the figure and are represented as open circles. The minimum reflectance of the structure was R = 1.64%, and was theoretically simulated as R = 1.69%. This shows that the theory is a close match to experimental results within  $\pm 3\%$ . However, there is a large difference between theory and experiment for very long wavelengths (12  $\mu$ m). This can be attributed due to being outside the transparency region of the films and different theoretical models would need to be used.



Figure 7.24: SEM cross-section of the final 6-layer PbTe/ZnO structure used for the single band AR coating



Figure 7.25: FTIR measured transmittance and reflectance of the final 6-layer PbTe/ZnO structure used for the single band AR coating

# 7.4.6 Experimental Results for High Power Infrared Lasers Operating Pulsed

High performance quantum cascade lasers (QCL) can be achieved through both improved material quality and advanced packaging techniques. The objective of this section was to determine the amount of optical confinement and output due to the reflectance values at the facets of the lasers. Many applications require lasers with short pulses and high peak power, and optical coatings can be used to achieve this by removing the limitation at the facets. Performance improvements due to HR coatings have been previously reported(201)(202). However, significant further improvements to the laser performance can be observed with the addition of high-quality AR coatings. This section demonstrates the effect that facet coatings have on achieving high peak output power  $P_{max}$  and high external efficiency  $\eta_w$  in pulsed operation.



Figure 7.26: Illustration of the AR and HR coatings on the facets used for high output power and high wall-plug efficiency for an infrared laser operating pulsed at roomtemperature

The lasers used in this work were similar to the lasers previously published in Ref. (203). The laser structure was designed to achieve the given objective by using a slightly higher average core doping of  $2.2 \times 10^{16} \text{ cm}^{-3}$ . The lasers were bonded epilayer up on copper submounts and measurements were tested at 298K with a pulse width of 500 ns at 100 kHz. The light was measured by a calibrated thermopile detector placed in close proximity to the laser. A different optical coating was deposited on each laser facet. The HR coating used was the same as structure discussed in Section 7.3.1, and the AR coating used was the same as the structure discussed in Section 7.4.5. An illustration of the coatings on the laser facets is given in Figure 7.26.

The reason why the facet coatings are efficient for achieving high output powers is because of the change in mirror loss of the laser. The mirror loss is related to the reflectance values at both facets and the cavity length of the laser by:

$$\alpha_m = \frac{1}{2L} ln[\frac{1}{R_{front}R_{rear}}] \tag{7.39}$$

Using asymmetric reflectance values, the power distribution must be considered and can be found equal to:

$$\beta = \frac{1 - R_{front}}{1 - R_{rear}} \sqrt{\frac{R_{rear}}{R_{front}}}$$
(7.40)

Any changes in mirror loss will lead to changes in the slope efficiency, and the impact it has is dependent on the internal loss of the laser and power distribution factor.

$$\eta_s = \frac{1}{(1+1/\beta)} \eta_i (\frac{\alpha_m}{\alpha_m + \alpha_i}) \tag{7.41}$$

The output power is then proportional to the slope efficiency. The relationship is given as:

$$P = \eta_s (I - I_{th}) \tag{7.42}$$

and this holds true prior to thermal roll-over.

The L-I-V curves of the 9.4  $\mu$ m QCL with four different combinations of optical coatings are provided in Figure 7.27. The four different combinations were: both facets uncoated, AR coated on the front facet only, HR coated on the rear facet only, and AR-HR coated facets. The first observable advantage to using an AR coating on the front facet is the improvement in the slope efficiency  $\eta_s$ . The slope efficiency difference between the four lasers was  $\eta_s = 701.4$  mW/A for the uncoated laser,  $\eta_s = 1389.4$  mW/A for the AR-only coated laser,  $\eta_s = 1090.9$  mW/A for the HR-only coated laser, and  $\eta_s = 1708.9$ mW/A for the AR-HR coated laser. This results in nearly 250% increase in the slope efficiency. As observed in the plot, one of the effects of the optical coatings is a change in mirror loss. The lower reflectance leads to a higher mirror loss which causes a shift in



Figure 7.27: L-I-V curves comparing a laser with different facet coatings. A 69% improvement in output power, 150% improvement in slope efficiency, and 69% improvement in wall-plug efficiency is achieved by using the proposed AR coating compared to one with an HR coating.

the threshold current density from  $J_{th} = 1.44 \text{ kA/cm}^2$  in the uncoated laser to  $J_{th} = 1.75 \text{ kA/cm}^2$  in the AR-HR coated laser.

Although there is a slight shift in the threshold current density, this becomes unimportant as long as the amount of power consumption is not a concern. As a result, the large slope efficiency leads to an increase by about 170% in maximum power from 0.94 W to 1.58 W. The percentage increase in maximum power is not the same percentage increase in slope efficiency, as would be expected from Eq. 7.42. The reason for this difference is because of self-heating effects due to larger operating currents, leading to a different behavior in thermal rollover. The combination of the increased threshold current density and increased slope efficiency cause the L-I curves of the HR-only and AR-HR coated lasers to intersect. In addition to higher  $P_{max}$ , a higher wall-plug efficiency was achieved with a 169% change from 2.35% to 4.28% due to the optical coatings.

In order to optimize the wall-plug efficiency, the optimal mirror loss for this laser was found to be  $\alpha_m^{opt} = 7.2 \text{ cm}^{-1}$ . When considering the appropriate choice for the combination of front facet reflectance and cavity length. This optimal mirror loss can be achieved through many different combinations of the front facet, rear facets, and the cavity length. In this situation, the rear facet should be as high as possible in order to minimize any complete light lost out of the laser. Therefore, an intermediary front facet reflectance and cavity length must be chosen. Simultaneously, the lowest front facet is desired while still achieving a maximum output power with a cavity length that is practically feasible. The optimal mirror loss can be achieved by choosing the same reflectance value with a cavity length of 3.11 mm

## 7.4.7 Anti-Reflection Coatings for Room-Temperature Continuous-wave Infrared Lasers

Improvements in output power have been previously demonstrated for mid-infrared lasers using AR coatings(204) and facet gratings(205) operating in pulsed mode at low duty cycles, however no work has been performed on the use of AR coatings for room temperature, high duty cycle lasers. The primary limitation for mid-infrared semiconductor lasers operating at high duty cycles and high temperatures is internal heating(206)(207), which requires proper advanced thermal management. Overcoming these heating effects is even more of a challenge for high duty cycle lasers with AR coatings because the lower reflectance on the front mirror facet causes a higher mirror loss and additional internal heating.

One major difference between mid-infrared and far-infrared QCLs is the significantly lower internal loss for the mid-infrared(208). The lower the loss, the more dominant the mirror loss is in influencing of the threshold current density. To explore this prediction, the change in threshold current density as a function of the facet reflectivities was experimentally compared for mid- and far-infrared QCLs. Figure 7.28 provides a plot of the pulsed, low duty cycle, threshold current density for different reflectance values. For a relative comparison, the data points were then fit to a logarithmic curve ( $J_{th} = a + b$  $\ln(R_{front})$ ). For the mid-infrared laser, the regression coefficients were a = 0.7238 and b= -0.3714, and for the far-infrared laser, the regression coefficients were a = 1.0769 and b= -0.1601I. This indicates that the shift in threshold current density is 2.3 times higher for the mid-infrared lasers.

To study the effects of the higher mirror loss on the performance, seven lasers were compared. All lasers are the same, but six of the seven have different reflectance values ranging from 0% to 22%, and the seventh laser had an uncoated front facet. The devices were  $\lambda = 4.6 \ \mu m$  lasers fabricated with a cavity length or 3 mm and bonded in an epilayer up configuration onto copper heatsinks. Measurements were performed using a calibrated thermopile with the laser operating at 100% duty at room-temperature.

The average powers of the lasers for duty cycles ranging from 5% to 100% were tested and are plotted in Figure 7.29. The optimal choice of front facet reflectivity was found



Figure 7.28: Threshold current density for different front facet reflectance values comparing the relative shift between mid- and far-infrared QCLs. This shows how the change in mirror loss due to the front facet reflectance has a more pronounced effect on the threshold current density for the MWIR laser due to its lower internal loss.

to be dependent on the operating duty cycle and targeted objective. The highest peak powers were obtained using the 0.86% AR coating. For duty cycles of 10 - 20%, the highest average powers were achieved with R = 10%, but for duty cycles greater than 40% up to 100%, the highest average powers were achieved using R = 15%. In this case the overall loss was  $\alpha_{total} = 3.7 \text{ cm}^{-1}$  and thermal conductance was found to be  $G_{th} = 227.5$ W/K-cm<sup>2</sup>. This resulted in a 24% improvement in output power and 20% improvement in wall-plug efficiency. Although the CW output power of the R = 22% AR coated laser is higher compared to the laser without a coating, even higher powers can be achieved with a slightly lower reflectance of R = 15%. This appears to be the optimal point where



Figure 7.29: Average power vs. duty cycle curves for the same laser with different AR coatings. A cross-over of the curves shows how the internal heating becomes a dominating issue for low reflectivity lasers at high duty cycles.

a higher amount of light is being extracted out of the laser cavity while still not being dominated by internal heating effects. The effects of the induced heating can be observed with the lasers having R = 10% and R = 12%. The average power was higher compared to the laser with R = 15% for lower duty cycles, where heating does not play as large a role in the performance. However, this is not the case for high duty cycles as can be observed with a cross-over of their curves.



Figure 7.30: P-I-V curves of the same AR-HR coated laser measured with two different pulse widths, both very narrow in duration, showing the large heat induced effects in the AR coated lasers

# 7.4.8 Anti-Reflection Coatings for External Cavity Tuning Systems

The performance improvements of AR coatings can not only be demonstrated in standalone lasers, but also in systems. One example is an external cavity tuning laser (ECL) system. The reason why AR coatings play a role with this is because it improves the amount of inter-cavity coupling. This leads to many performance improvements such as wider tuning range, higher current operation, higher output powers, and mode hop-free tuning. The optical coating suppresses mode competition so this allows for single-mode operation of the layer system(209). There have been a few reports using single-layer AR coatings in the ECL system, but the reflectance is not as low(210) and the coupling is not very high(211)(212)(213).

The ECL system used in this work is shown in Figure 7.31, setup in a Littrow Cavity configuration. The lasers used were similar to Ref. (207), with a wavelength at  $\lambda \sim 4.7$   $\mu$ m when stand-alone. They were bonded to copper epi-layer up onto copper submounts and tested at T = 298 K at a 100% duty cycle. A metallic HR coating was deposited on the rear facet, and a 15 nm ZnSe, 230 nm Y<sub>2</sub>O<sub>3</sub> double stack structure was deposited on the front facet of one laser for an AR coating. A reflectance of R = 0.86% was measured, as shown in Figure 7.32.



Figure 7.31: Illustration and photograph of the external cavity tuning system used in this work

At 10% above threshold, the tuning range showed nearly a three-fold improvement from 125 nm to 350 nm. This is shown in Figure 7.33. With this improvements, the detection of carbon monoxide(214) and acetylene(215) can now be possible. As the operating current became higher, mode hopping started to became an issue for the ECL system with the HR-only coated laser. As a result, the tuning range of 125 nm was not achieving at the maximum operating current. This was not the case when the ECL system



Figure 7.32: FTIR measured transmittance and reflectance of the AR coating structure, where a reflectance of R = 0.86% is used for a  $\lambda \sim 4.7 \ \mu m$  laser.

used the AR-coated laser, demonstrating the capabilities of high power tuning.

A significant problem with AR coatings reported in the literature is that the thermal expansion coefficients of the laser facet and dielectric are significantly different. Problems with peeling or flaking of the coating have been reported to be a problem due to the mismatch(211). To measure the robustness of the coatings used in this work, thermal cycling tests were performed. One cycle consisted of cooling the laser from room temperature to 80K in a cryostat and heating it back up to room temperature. The cooling rate was 15.3 K/min and the heating rate was 17.8 K/min, which are the fastest rates allowed by the cryostat. The P-I-V curve of the laser was measured after each cycle. The AR coating withstood at least 75 cycles without any changes in the P-I-V curves.



Figure 7.33: Wavelength tuning achieved with an external cavity tuning system compared without and with an AR coating on the front facet of the laser. A wider tuning range is achieved when using an AR coating on the front facet, from 125 nm to 350 nm.

This is typically a sufficient number of cycles to observe significant deterioration or even complete failure of the coating. A slight amount of peeling was observed where defects were present on the facet, however, the defects were located far away from the active region of the laser, and therefore had no effect on the performance. A comparison of the photographs of the facets viewed under SEM are given in Figure 7.34.



Figure 7.34: SEM of the AR coated laser facet before and after thermal cycling exhibited no signs of thermal expansion or peeling except in areas where defects were present on the substrate.

# 7.5 Two-Dimensional Narrowband Anti-Reflection Coatings

The two-dimensional narrowband AR coating is different from the single band AR coating described in the previous section in that a restriction is placed on the width of the peak transmittance. This section provides information on how to design such a structure and discusses some of the future potential issues.

### 7.5.1 Background

An edge emitting lasers is a two-dimensional divergent source. An example far-field measurement of a laser, Figure 7.36, shows a divergence of around 30° away from normal incidence. This can lead to large amount of loss for applications such as free space

communications where the amount of loss becomes significant as the distance gets larger. The angle of transmittance is related to the angle of incidence by Snell's law for different substrate refractive indices as shown in Figure 7.37. By observing the angle of incidence graph, it can be determined that the angle of incidence at the facet interface is around 60°. Therefore, the angle of transmittance or beam divergence can be collimated by restricting the angle of incidence. This is illustrated in Figure 7.35, comparing the beam shape with and without the narrow bandpass. This means that the direct goal is to limit the angle of incidence to be as close to normal as possible. The angle of incident light cannot be controlled, so instead the angles allowed to transmit through is controlled. The angles can be selectively chosen such that far from normal incidence angles will reflect back into the cavity, instead of transmitting through and being lost due to the large divergence



Figure 7.35: Illustration of the change in beam shape expected from a narrow bandpass AR coating

To control the angles transmitted and for proper characterization, a narrow bandpass can be used. The reason why this is effective is because a non-normal angle of incidence causes a shift in its towards shorter wavelengths, related by:

$$\lambda_{\theta} = \lambda_0 \sqrt{1 - \frac{n_0}{n_{AR}} \sin^2 \theta} \tag{7.43}$$



Figure 7.36: Measured far-field from a standard laser showing a divergence of about 30 from normal

Therefore, larger angles will lead to a broader transmittance band.

There are many ways to develop a narrow bandpass structure(216). The difficulty is the compromises made between transmittance and bandwidth. The procedure used involved choosing an initial structure and using an algorithm to optimize it. Two materials were chosen: one with a low and one with a high refractive index. With this, two passbands were constructed: one was a short-wave passband and the other was a long-wave passband. They were layered one passband next to another and the goal was to have each passband perform its designed rejection. The merge of the two passbands is shown in Figure 7.38. Iterations were then performed with modifications on both refractive indices and thickness of the layers. Once the convergence process was complete, neighboring layers that were



Figure 7.37: Relationship between angle of transmittance and angle of incidence for a substrate with a refractive index between 3.3 and 3.8. One way to control to collimating the beam shape is by restricting only certain angles of incidence to transmit out of the laser facet.

made of the same materials were then be merged into one layer, so the total number of layers was then reduced.

The search procedure used was a probabilistic algorithm called Simulated Annealing (217)(218). It is most commonly used to reach a global optimum for a large search space, and its main advantage is avoidance of being trapped in a local minima. Each step in the algorithm involves randomly perturbing the current structure to create a new structure. The merit function is calculated, and the decision of accepting the new structure is based on the probability:

$$p = \exp(\frac{-\delta M}{T}) \tag{7.44}$$



Figure 7.38: The formation of a narrow bandpass which was done using both a short-wave passband and a long-wave passband in series. Incident light outside of the wavelength range will be rejected by either one.

where  $\delta M$  is the change in merit function and T is a control variable. For a given T, the probability of accepting a move is lower if the change in merit function is high.

The parameter T was set initially to be high in value and decreases with iterations. When the parameter T was high, the bias towards choosing the structure with improved merit function was low. This allowed exploration of the entire search space, and as a result there was a higher probability that structures with worse merit function was chosen to prevent being stuck at a local minimum. Incrementally, the T value was decreased  $T_{k+1}$  $= \alpha T_k$  where  $0 < \alpha < 1$ . With lowering of T, the probability of accepting a structure with worse merit function became small so most moves would lead to a local minima convergence. Finally, the algorithm was terminated after no more moves were made.
### 7.5.2 Experimental Design and Procedure

The procedure for design of the narrow bandpass AR coating was discussed in the previous section. In this example, the targeted objective was for a  $\lambda \sim 4.6 \ \mu m$  laser. Three designs were deposited and compared where differences were made with its merit function. The main objectives were highest transmittance, narrowest band, or simultaneous high transmittance and narrow band. There were three restrictions made on all three designs, and that is maximum transmittance greater than 80%, FWHM less than 500 nm, and thickness less than 2  $\mu m$ . Any structure that did not meet all three requirements were discarded, and the resulting structures are shown in Figure 7.39. The NB #1 structure had 123.1 nm ZnSe, 196.7 nm Y<sub>2</sub>O<sub>3</sub>, 250.2 nm ZnSe, 199.7 nm Y<sub>2</sub>O<sub>3</sub>, 127.8 nm ZnSe, and 199.1 nm SiO<sub>2</sub>. NB #2 consisted of (ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/Y<sub>2</sub>O<sub>3</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/ZnO/SiO<sub>2</sub>/Zn

409.7/106.3). NB #3 was a 12 layer  $(TiO_2/Si_3N_4/PbTe/Si_3N_4/PbTe/Si_3N_4/PbTe/Si_3N_4/PbTe/Si_3N_4/PbTe/Si_3N_4)$  with thickness values of (17.2/43.8/34.3/45.2/31.6/48.1/33.7/12.0/25.6/67.1/19.6/25.6).

Each of the three structures was deposited and characterized. The characterization results are given in Figures 7.40, 7.41, and 7.42. A summary of the results are provided in Table 7.4 with bandwidth number reported based on the width at T = 73%. NB #1 was not chosen because it exhibited poor optical spectra with transmittance values only slightly higher than 80%. NB #2 was not chosen due to the stress and microstructural



Figure 7.39: Optimal narrow bandpass AR coating structures. They were designed by using an initial series stack of both a low pass and high pass filter with refinement made by using a simulated annealing algorithm. The three structures each had a difference in main objective: highest transmittance, most narrow band, and simultaneous high transmittance and narrow band.

issues observed with the SEM figure. Due to the tremendous number of layers and high compressive stress, it was predicted that this film would mechanically fail when either applied to the laser facet or after thermal cycling tests. Finally, NB #3 was chosen due to its very nice transmittance curve with narrow peak transmittance wavelength range span of about 200 nm. Although the AFM scan did not exhibit the best surface morphology, the FTIR curve proved an insignificant amount of light lost due to light scattering. Optimization could have been made on this structure in order to reduce the morphology and potentially make the peak transmittance have a higher intensity, however this action was not taken due to the sensitivity of the bandwidth.

Narrowband #1	
AFM	Small grain sizes. Measured RMS roughness of 0.783 nm
SEM	Very nice, smooth interfaces. Layers were comparatively thick and were relatively the same in thickness value.
FTIR	Peak wavelength slightly shorter than desired, occurring around $\lambda \sim 3.8 \ \mu m$ . Bandwidth spans a wide range of about 1 $\mu m$ . This translates to about 33.8° divergence from normal. The solution of increasing layer thickness in equal amounts of ratios is not applicable in this situation. This would lead to changes in both peak transmittance value and bandwidth
Narrowband $\#2$	
AFM	Extraordinarily small grain sizes and very smooth surface. RMS roughness was measured as $0.350$ nm.
SEM	Good interface quality, but poor microstructure observed in ZnO layers. The microstructure and complexity may lead to issues with film stress
FTIR	Low peak transmittance of $T = 81.3\%$ , occurring at a shorter wavelength of 3.8 $\mu$ m. Bandwidth spans a range of about 500 nm, translating to 13.2° divergence from normal. The divergence is improved compared to an uncontrolled beam, but the transmittance value is very low.
Narrowband #3	
AFM	Larger grain sizes that are elliptical or oval shaped. Areas of light trapping are not periodic and instead having varying sizes and shapes.
SEM	Good interfaces. Contrast of layers is not as bright as NB $\#1$
FTIR	Very narrow bandwidth of 200 nm with peak transmittance value of T = 96% very close to the targeted.

Table 7.4: Summary of the characterization results from deposition of three different narrow bandpass structures.



Figure 7.40: AFM scans of the three narrow-band AR coating structures



Figure 7.41: SEM of the three narrow-band AR coating structures

# 7.5.3 Theoretical Predictions and Future Work for High Wall-Plug Efficiency Infrared Lasers

The objective of this section was to use AR coatings to control the properties of the beam output by allowing only certain angles of incidence to transmit through. A plot comparing a single band AR coating, designed using the procedures given in Section 7.4, with the narrowband coating is given in Figure 7.43. Both designs had a targeted wavelength of  $\lambda \sim 4.7 \mu m$ , and the differences in bandwidth at this wavelength are significant. From the bandwidth and Eq. 7.4, the predicted divergence of the collimated beam is 2.3 times



Figure 7.42: Comparison of the FTIR measured transmittance of the three narrow bandpass structures

lower leading to an improvement in wall-plug efficiency of about 30%.

Future work involves depositing this structure on a laser facet and measuring its performance. While this is expected to improve the beam divergence, and therefore the wall-plug efficiency, there are a few predicted challenges that will be encountered and may need to be considered. The first is the shift in wavelength of the laser with temperature and its relative comparison to the shift of the structure. Any mismatch in values between the two can lead to reduced performance. The second major factor that needs to be considered is the eigenmode of the laser, which may operate outside of the wavelength range of the narrowband. The transmitted portion of the mode may overlap with the reflected portion leading to not optimized conditions. Another factor that should be taken into account is the dependence of the laser waveguide geometry on the output



Figure 7.43: Comparison of a single band AR coating structure with a narrow band coating structure exhibited the significant difference in bandwidth

of the narrowband AR coating. An example is the optimal phase of the narrowband AR coating is expected to shift to lower values with wider ridges(219). Finally, the last characteristic that may need to be considered is the polarization, as the design presented in this section was for a TM-polarized laser. It must be noted that more challenges may arise and these challenges can lead to incorrect predictions with the performance improvements.

# 7.6 Broadband Anti-Reflection Coatings

The broadband AR coating is similar to both the single band and narrow band AR coatings in that the highest transmittance is desired. However, for the broadband coating,

a second objective is to allow transmittance over a wide range of wavelengths. This section will provide information on how to design such a structure.

## 7.6.1 Background

The ability to achieve zero percent reflectance over a wide range of wavelengths can be done by considering the phase of the structure. A way of doing this is by using a graded refractive index that varies from the refractive index of the substrate at one end of the structure to the refractive index of the ambient, or in this case air, in the other structure. The reason why this is effective is because a specific phase corresponds to achieving a zero percent reflectance at a specific wavelength. Then the utilization of a wide range of refractive indices, or in other words phase values, will lead to the wide span of zero percent reflectance.

The simplest way to determine the variation in the refractive index across the structure is to vary it linearly, as shown by the dashed line in Figure 7.44. There are other variations in the refractive index that can be used to achieve a better initial solution(220), but the use of an efficient optimization algorithm made the difference have a negligible impact. Since designing a structure with perfect inhomogeneity or variation across it can be very difficult, one way to represent this is by breaking up the structure into multiple layers L. Each layer is then assigned a refractive index value that corresponds to the half-way point  $((n_{i+1}-n_i)/2) + n_i$ . In general, the greater the number of initial layers L that is used will result in not only a better initial solution, but also more flexibility with the optimization that will be used later on.



Figure 7.44: Illustration showing the variation of the refractive index in the broadband AR coating structure. The dashed line represents the initial linear relationship. Filled circles are the actual refractive index values after breaking up the structure into layers, assigned as half-way in-between

Once the layers are broken up and the appropriate refractive index values are assigned, any layer with an unrealizable refractive index is substituted by its three-layer equivalent. Details on how the substitution is performed are given in Section 7.2. Finally, the structure is then optimized by using a flip-flop method. Each layer is traversed and the layer is replaced with a different material. If the performance of the structure after the flip results in an improved merit function, then the change is kept. Otherwise, any worsening of the performance will lead to the change being discarded. After one pass through all the layers, the layer thicknesses are then incrementally adjusted, and the optimization terminates when a pass through all the layers leads to no changes.

### 7.6.2 Experimental Design and Procedure

The procedure used for developing the broadband coating structures were given in the previous section. In this example, the broadband AR coating was designed with a targeted refractive index of  $n_{target} = 1.93$ . An illustration of the final three structures are given in Figure 7.45. Structure A involves PbTe,  $Y_2O_3$ , and ZnO materials. The individual layers and thicknesses starting from the bottom of the structure adjacent to the detector surface were (179.4/31.8/158.2/41.3/42.0/68.0/120.3/29.7/143.9/10.2/432.5/3.6/429.6) in nm with materials of  $(Y_2O_3/PbTe/Y_2O_3/PbTe/ZnO/Y_2O_3/ZnO/Y_2O_3/ZnO/PbTe/ZnO/Y_2O_3/ZnO)$ . The layers of Structure B were (119.4/11.8/138.2/41.3/128.7/82.0/68.1/130.3/29.7/153.9/2.6/321.1/4.8/320.5/4.4/328.1) in nm with materials of  $(Si_3N_4/PbTe/Si_3N_4/PbTe/Si_3N_4$  $/SiO_2/Si_3N_4/SiO_2/PbTe/SiO_2/Si_3N_4/SiO_2/Si_3N_4/SiO_2/Si_3N_4/SiO_2)$ . Structure C consisted of the most number of layers of all three broadband AR coatings. The structure total thickness of  $1.33 \ \mu m$  from individual layers of  $(ZnO/PbTe/TiO_2/PbTe/TiO_2/ZnO/$  $TiO_2/ZnO/TiO_2/ZnO/PbTe/ZnO/PbTe/ZnO)$  with thickness in nm of (140.1/19.2

/130.8/32.9/107.1/67.4/72.6/102.6/37.4/128.3/11.7/149.2/2.8/322.7)

A summary of the characterization results are given in Table 7.5. The AFM scans of the three structures are shown in Figure 7.46. The grain shape and sizes of all three structures were significantly different. Structure A had a very smooth surface, whereas structure C showed very large grains with what appears to be incomplete coalescence. Structure B showed medium-sized grains with occasional peaks spaced approximately 300 nm apart.



Figure 7.45: Optimal broadband AR coating structure designs determined using an initial graded-index structure with modifications made from a flip-flop optimization algorithm. The three structures each had a difference in its main objective: high transmittance, widest band, and simultaneous high transmittance with a wide band

The cross-sections viewed under SEM for all three structures are given in Figure 7.47. For structure A, the microstructure of the individual layers were good and no obvious grain boundaries or voids were observed. However, the interfacial quality is not ideal. Jagged interfaces are observed, beginning with the first layer of  $Y_2O_3$ . For structure B, the SEM cross-section showed good quality in both the individual layers' microstructure and interface quality in-between. Finally, odd vertical columns were observed in the microstructure of structure C. This is speculated due to both TiO<sub>2</sub> and ZnO materials.



Figure 7.46: AFM scans of broadband AR coating structures



Figure 7.47: SEM of broadband AR coating structures

A comparison of FTIR measurements from the three structures is given in Figure 7.48. The highest transmittance values were exhibited with both Structure A and Structure B. The values were both around 95% with a difference of less than 1%, however a difference in wavelength of peak transmittance was significant. Structure B was mainly chosen as the ideal structure due to its peak transmittance being located at  $\lambda \sim 4.8 \ \mu m$  with good broadband behavior. Greater than 90% transmittance can be achieved over a span of 4  $\mu$ m, with a gradual and slight decrease at the longer wavelengths. At  $\lambda \sim 7.6 \ \mu$ m, the structure becomes ineffective in achieving high transmittance and this is due to the absorption of SiO<sub>2</sub>. Substitution of this material with one that is transparent is expected to eliminate this drop in transmittance. Finally, structure C was not chosen due to its optical spectra. Transmittance values were below 75% for wavelengths longer than 5  $\mu$ m.

#### Broadband A

- AFM Very smooth surface morphology with small grain sizes observed
- SEM Cross-section of the structure looks very nice, but the interface quality appears to be slightly affected.
- FTIR High transmittance with peak value around T = 93%, but a dip in value down to 81% is observed for wavelengths between  $\lambda \sim 4.2$  - 7.4 µm.

#### Broadband B

- AFM Small grain sizes with occasional surface spikes spaced approximately 250 300 nm apart.
- SEM Material microstructure and very good interfaces observed
- FTIR High transmittance with a peak value of T = 95.3% located at 4.8  $\mu$ m. Good broadband behavior spanning 4  $\mu$ m is observed with a slight and gradual decrease in transmittance for the longer wavelengths. AR coating becomes ineffective beyond 7.6  $\mu$ m due to SiO<sub>2</sub> absorption

### Broadband C

- AFM Very large, randomly sized grains. The AFM scans show incomplete coalescence of the microstructure.
- SEM Poor columnar microstructure observed, especially at the top of the AR coating. This is due to the majority of the structure containing ZnO. Conditions of ZnO would need to be optimized to account for this issue, but doing so may also alter the optical properties of the material.
- FTIR The structure shows both very low transmittance and poor broadband behavior.

Table 7.5: Summary of the characterization results from deposition of three different broadband structures.



Figure 7.48: FTIR measured transmittance of the three broadband AR coating structures

# 7.6.3 Experimental Results for High Quantum Efficiency Room Temperature Infrared Detectors

The role of the AR coatings for detectors is to remove the limitation that only  $\sim 75\%$  of the light can transmit through to the semiconductor. So, the objective was to achieve as high a transmittance as possible over a broad spin of wavelengths. This section demonstrates how the AR coatings can be used to achieve high quantum efficiency detectors.

The AR coatings were deposited on the top-side of Type-II InAs/GaSb superlattice photodetectors with a 50% cutoff wavelength at  $\lambda_c$ , 50% ~ 7 µm similar to Ref. (221). Before deposition, the samples were processed using standard UV photolithography. Top metal contacts consisting of Ti/Pt/Au/Ti were deposited by electron beam evaporation, and the AR coating was then deposited on top. Windows were opened by using a CF<sub>4</sub>based dry etch. The detectors were bonded to a chip carrier and quantum efficiency



Figure 7.49: Illustration of broadband AR coatings for high quantum efficiency on an infrared detector utilizing top-side illumination.

measurements taken at T = 300 K. An illustration of the AR coating on the detector is given in Figure 7.49.

The reason why AR coatings are effective for high quantum efficiency is because it is directly related to the reflectance by:

$$\eta = (1 - R)(1 - \frac{\exp[-\alpha W]}{1 + \alpha L_D})$$
(7.45)

where  $\alpha$  is the absorption, W is the depletion width, and  $L_D$  is the Debye length. Therefore, the reflectance is proportional to the quantum efficiency and lower reflectance values will allow more incident light to transmit to the detector.

The AR coating structure chosen from the previous section was structure B, and this choice was made based on the high transmittance value, broad wavelength span, and ease with etching for openings to metal contacts. The experimentally measured FTIR is plotted in Figure 7.50. The figure also provides in the theoretically simulated curve shown in the open red circles, and a good match of less than 5% difference was observed between experimental and theoretical. Finally, Figure 7.51 provides the comparison of quantum

efficiency for a detector with and without the AR coating for top-side illumination. Up to 62% improvement in quantum efficiency is observed due to the increased detectivity by allowing the maximum amount of radiation to penetration through to the semiconductor. Further, as can be seen in Figure 7.53 and Figure 7.53, the thermal expansion of the structure is minimal which is important when cooling the detector down to very low temperatures. Any changes due to thermal expansion can lead to unwanted effects such as peeling.



Figure 7.50: FTIR measured transmittance of the broadband AR coating structure and a plot of the theoretical simulation model within 5% error



Figure 7.51: Demonstrated improvement in quantum efficiency of an infrared detector operating at room temperature due to utilization of the broadband AR coating structure on the top-side

# 7.7 Experimental Challenges

There were three main challenges faced during the experimental deposition and integration of the AR coatings with the devices. This includes ion-induced heating effects, dielectric breakdown, and film buckling. Solutions to these issues have been found and will be provided in this section.

## 7.7.1 Ion-Induced Heating Effects

As discussed in Section 2.3.6, an increase in the substrate surface is expected due to the ion bombardment during the deposition. This induced heating may become a significant



Figure 7.52: Shift in transmittance of the AR coating structure with temperature. An increase in value occurs with lower temperatures, due to a change in the refractive index and a slight shift towards higher frequencies occurs.

problem, especially for processes sensitive to temperature. One challenge faced during the work discussed in this chapter was the change in electrical properties of the laser due to the higher induced surface temperature at the facet. The high temperature was found to degrade the oxide-to-gold interface adhesion for either the gold on top of the ridge waveguide, gold on rear facet HR coating, or both for the lasers. The result was a worsening of the electrical I-V curves and a loss of optical power through the rear facet. Figure 7.54 provides the L-I-V curves of a laser, both with an HR coating deposited on the rear facet, with and without an AR coating deposited after the HR coating. There should be no change in the I-V curve between the laser before and after the AR coating, but the plot shows a clear drop in resistance. In addition to the current leakage change with the



Figure 7.53: A graph showing the trend in the change in structure properties due to thermal and optical expansion of the material to the substrate.

I-V curve, the L-I curve shows the proper threshold current density shift, as predicted by theory, but a significant degradation in output power occurs. The slope efficiency of the AR-HR coated laser should be higher than the slope efficiency of the HR-only coated laser, which is not the case for this situation.

In order to isolate the problem, the AR coating was deposited on the HR coating laser with three different attempts. The structure was the same for all attempts with the only differences with the amount of time the laser is allowed to cool down during the deposition. The P-I-V curves are shown in Figure 7.54 with the ideal curve labeled as no gold degradation. AR coating #1 was deposited continuously without any opportunities for the laser to cool down and AR coating #2 was deposited in 30 minute segments



Figure 7.54: (a) L-I-V curves of a laser with change in electrical properties with and without AR coating deposited by IBSD. (b) P-I-V curves of three identical lasers with same AR coating, but with differences in the fabrication sequence. AR Coating #2 is the same as AR Coating #1 with the deposition divided into multiple processes to allow the laser to cool down.

separated by 2 hours of cooling time. The slight improvement observed with AR coating #2 indicates the presence of a heating problem. A third coating structure was made with shorter deposition segments of 10 minutes and longer cooling segments of 5 hours. Although there was a clear indication of the presence of a heating problem, it still could not be completely eliminated by taking this approach. Instead, a solution to overcome this problem was by modifying the fabrication sequence. The resulting L-I-V curve matched with the ideal when the AR coating was deposited prior to the HR coating, ensuring that the gold deposition is the last step in the processing sequence. This dependence leads to the belief that the oxide-to-Au interface degradation problem exists in the HR coating and not with the gold on the top of the ridge waveguide. While there are no actual fundamental differences in how the deposition of the dielectric and gold for both the HR

coating structure and ridge waveguide is done, the reasoning for the insignificant effect on gold for the ridge waveguide may be due to either the presence of the electroplated gold or the difference in surface area coverage.

## 7.7.2 Dielectric Breakdown

Another challenge with the deposition of the AR coating structural involves the structural density of the films. As the reflectance of the front facet decreases, the maximum power coming out of the facet becomes greater. The AR coating structure must be able to structurally withstand this high power. This power translates to a high voltage being applied across the AR coating structure. If the structure is not robust enough, one or two weak spots will form. The weak spots are due to the breakdown of the material, which leads to loss of the electrical isolation properties of the material. The breakdown of the material then allows a current to flow through it, causing localized heating and, as a result, induce a larger amount of current flow. The larger current flow leads to more localized heating, and a cycle continues between the two effects until a "hot spot" has formed from melting of the material. It is, therefore, important to deposit films with a high dielectric breakdown strength. To measure the dielectric breakdown strength, I-V curves can be taken until the voltage is high such that the curves begin to exhibit a behavior, similar to what is shown in Figure 7.55. There is an abrupt jump in the current value at breakdown, and for voltages greater than this, the behavior follows that of the substrate.

An SEM picture of the facet after dielectric breakdown with the hole burning is shown



Figure 7.55: I-V curves of  $\text{TiO}_2$  showing dielectric breakdown for one contact around 18.8 V and the other contact around 24.2 V. This translates to a breakdown voltage between 188 - 242 MV-cm<sup>-1</sup>.



Figure 7.56: SEM pictures of a laser facet that has experienced breakdown for very high output power densities. The breakdown is due to the localized heating that occurs in the AR coating structure, as can be observed.

in Figure 7.56. A closer SEM scan of the hot spots is shown in Figure 7.57. Since it could not be determined from the SEM graph whether the circular features were a depression or indentation, the surface of the facet was scanned using AFM. The AFM scan shows the two circular features as bumps that protrude out of the surface with a size of approximately 1.5  $\mu$ m x 2  $\mu$ m and a height of approximately 600 nm. Near the circular features are smaller bumps and hills, which may be attributed due to the eruption of the gold metal contact onto the facet surface.

The hole burning problem was found due to using an AR coating structure with low breakdown, which was related to its porosity. Therefore, the solution to this was to use films with a very high packing density. The methods to achieving high packing density can be done so by using the secondary RF source and the energy of the incoming target atoms, as discussed in Section 6.1.1. Further, high density films are typically achieved with small grain sizes and small packing between grains, so prevention of coalescence can become a helping factor.



Figure 7.57: 10  $\mu$ m x 10  $\mu$ m AFM scan of the two circular features observed on the laser facet. The two circular features elevated as bumps with a height of approximately 600 nm.

## 7.7.3 Film Buckling

Film buckling refers to the process when the film undergoes spontaneous lateral deflection over the debonded area. An example is shown in Figure 7.58 showing a debonded portion from the substrate. The buckled part still exerts forces on the attached portion and whether this stays intact depends on the post-buckling handling of the films. If this does not stay attached, then the top-side of the film begins to look like what was observed in the optical microscope.



Figure 7.58: SEM picture and optical microscope view of film buckling due to high compressive stress

The amount of tolerable compressive stress before a buckle is induced proportional to both the energy and height of the film, and it is inversely proportional to the area of the debonded zone. This information can be adjusted for when depositing of the materials if modifications in the material properties for lower compressive stress is undesired. Changes in compressive stress were discussed in Section 6.1.2, but a simpler solution would be to deposit layers with lower thickness values.

# 7.8 Summary

This chapter discussed and showed the performance improvements of optoelectronic devices due to the application of optical coatings. The problem was that the percentage of incident radiation was limited to about 70 - 75% of the maximum intensity due to the refractive index difference between the semiconductor and air. A hypothesis was presented that optical coating structures can be designed to achieve a higher transmittance and enhance the performance of the devices. Four different types of coating structures were discussed: HR, single-band AR, narrowband AR, and broadband AR. Two different types of HR coatings were detailed: metallic and dielectric stack. The metallic HR structure is advantageous because of being simple and having a high probability of achieving near 100% reflectance. However, it is limited in attainable reflectance percentage values, so the dielectric HR coating structure was presented as a resolution.

The three different AR coating structures all had the same objective of achieving as high a transmittance value as possible. The only difference between the three was the extra requirements where narrowband AR required the max transmittance to occur over a narrow span of wavelengths and broadband had an opposite requirement of a broad wavelength range. Both the single band and narrowband were used on infrared lasers with motives of achieving a higher output power for the single band and higher wallplug efficiency for the narrowband. On the other hand, the broadband AR coating was demonstrated on an infrared detector with performance improvements demonstrated with higher quantum efficiency values. Finally, solutions were given to three of the major experimental challenges that were faced. These challenges included induced heating effects due to continual bombardment of the high energy ions, dielectric breakdown for high output power densities, and film buckling due to high compressive stress.

# **CHAPTER 8**

# Surface Passivation

This chapter discusses the utilization of dielectric materials for successful passivation of the surface of the optoelectronic devices. Due to the sensitivity of the devices, the problem is that the behavior of the devices is often limited by the poor structural, electrical, and optical quality of the materials at the interface, so the objective is to tune the characteristics of the dielectric in order to meet specific objectives to alleviate any issues. Three different properties are explored: structural, electrical, and optical. After each one is discussed, challenges and solutions that were encountered during experimental proof of the hypothesis are given in Section 8.4.

# 8.1 Structural Passivation

The objective of structural passivation was to demonstrate structurally robust lasers. This section will provide the background, material selection, design and procedure, and results on how this was done by considering the electric field intensity distribution.

#### 8.1.1 Background

High output power lasers are required for many different applications. In almost all cases, a high-reflection coating is needed in order to prevent light loss out of one end of the laser. However one problem is that at higher output power densities, the coating is unable to withstand this. This is because breakdown of the optical coating occurs and can lead to inoperability of the laser.

The cycle of problems that occurs is shown in Figure 8.1. The main source of breakdown is localized heating(222), coming from two main sources. The first source is located at the semiconductor-dielectric interface where dangling bonds and defects can be present. The second source is in the dielectric material itself, where absorption can also occur. As photons become absorbed, this gives the electrons extra energy to jump the bandgap and causes the generation of electron-hole pairs. The result of the electron-hole pairs is nonradiative recombination which leads to localized heating. The localized heating then causes a reduction in bandgap, and this reduction can either increase the carrier concentration or cause more absorption of light. The cycle continues until eventually the localized heating becomes too much and causes breakdown.

The design of the optical coating structure is done by not only considering the reflectance value, but also considering the absorption at both the interface and the material itself. Absorption of radiation at a given point has been found to be related to its electric field intensity(EFI). Therefore, the design is based on suppressing the maximum EFI to areas with highest resistance(223). In order to tailor the design to appropriate distribu-



Figure 8.1: Cycle illustrating the process from absorption of light to breakdown that occurs in HR coatings

tion of the EFI, knowing the behavior of the electric field at any point within the coating structure is needed. This was done by iterative simulation starting with the known intensity at the point of incidence entering into the structure. Then the value at each interface is calculated with the tangential component being continuous across the boundary. The total EFI is found then by summing the intensity transmitted through the boundary and the intensity reflected from the boundary. Within each layer, the transmitted and reflected EFI at a given depth from the interface is given as(224)(225)(226):

$$E_i^+(z_i) = \frac{1}{t_{ij}} \exp[-i\delta_i(z_i)] E_j^+(0) + \frac{r_{ij}}{t_{ij}} \exp[-i\delta_i(z_i)] E_j^-(0)$$
(8.1)

$$E_i^-(z_i) = \frac{r_{ij}}{t_{ij}} \exp[i\delta_i(z_i)] E_j^+(0) + \frac{1}{t_{ij}} \exp[i\delta_i(z_i)] E_j^-(0)$$
(8.2)

where  $z_i$  is the thickness within layer i from interface j,  $t_{ij}$  and  $r_{ij}$  are the transmission and reflection coefficients at the interface between layer i and layer j, and  $\delta_i$  is the phase change through layer i.

## 8.1.2 Material Selection and Design

The current solution for HR coatings is to use a metallic HR structure, as discussed in Section 7.3.1. However, the problem with this design is the low threshold for breakdown. The main breakdown mechanism within the entire structure is due to the extremely high EFI which originates from the strong refractive index of the metal. In this case, the metal used was gold. Other metals can be used, such as nickel, to produce the high reflection values. However, the extinction coefficient values are still too high. Therefore, the design presented as a solution to breakdown is based on the dielectric HR coating discussed in Section 7.3.2.

There are three main objectives: low defect density at the semiconductor-dielectric interface, low absorption coefficient within the structure, and high reflectance value. For the first objective, consideration of the number of dangling bonds and defect density at the semiconductor-dielectric interface is important since the EFI exhibits at least a local maximum in this area. The interface quality is dependent on not only the dielectric material, but also the deposition conditions. One common problem with IBSD is the surface damage or creation of surface states due to the high energy ions. Solutions and alternatives to this issue are discussed in Section 8.4.2. Figure 8.2 shows why TiO<sub>2</sub> was chosen as the first material with its PL intensity being the highest after annealing.



Figure 8.2: (a) PL intensity comparing the six different materials for lowest number of interfacial states. Plots with dashed lines were annealed in  $N_2$  at 500 °C for 5 minutes and solid lines were not annealed. (b)HR coating structure designed for high resistance breakdown to high output power densities, designed by appropriate material selection and distribution of the electric field intensity.

The second objective is to achieve low absorption inside the material itself to reduce the number of electron-hole pairs. Each material has several absorption bands that are characteristic to the material. Since these bands are characteristic, they cannot be avoided and therefore materials that exhibit large coefficient values in the wavelength of interest should not be chosen. Two example materials are  $SiO_2$  and  $Si_3N_4$ , and their absorption spectra can be found with Figure 4.6 and Figure 4.9.

With the considerations of the two objectives mentioned earlier, the third objective can be met by considering the phase change of light in order to achieve a high reflectance value. The initial structure chosen was a dielectric stack HR coating with quarter-wave thick layers of alternating high and low refractive indices. A larger difference between the two refractive indices typically leads to higher reflectance values. Due to its high refractive index value and transparency, PbTe was chosen as the high index material.

### 8.1.3 Experimental Results for Structurally Robust Infrared Lasers

The three objectives discussed earlier led to material selection of TiO<sub>2</sub> immediately adjacent to the laser facet,  $Y_2O_3$  for the low refractive index layers, and PbTe for the high refractive index layers. A fourth material was added and this was because the targeted wavelength of 10  $\mu$ m required thick layers in order to achieve a quarter-wave. This leads to the potential problem of film buckling and peeling. With the  $Y_2O_3$  layers being the thickest, they were divided into multiple thin layers with very thin separation layers inserted in-between. For the separation layers, the appropriate material must have a thermal expansion coefficient and refractive index close to that of  $Y_2O_3$ . These requirements are enforced to prevent any extra absorption at the  $Y_2O_3$  may require used to separate the TiO<sub>2</sub>.

The end result is the design shown in Figure 8.3. The design meets all four requirements of low interfacial defects, low material absorption, high reflectance, and low compressive stress. From this design, the resulting simulated EFI can be found in Figure 8.4. The intensity located immediately at the laser facet is typically one of the weaker areas. Emphasis was made to reduce the EFI at the facet interface, and the only way to do this is if the max EFI was relocated to the nearest  $Y_2O_3$  segment.



Figure 8.3: SEM of the structural passivation structure



Figure 8.4: (a)Plot of the electric field intensity in both types of HR coatings showing a significantly higher value in the metal gold layer due to its refractive index. (b)Simulated electric field intensity of the dielectric HR coating designed for structural robustness

# 8.2 Electrical Passivation

The objective of this section was to achieve close-to-bulk  $R_0A$  values with infrared detectors. This section will provide the background, material selection, and results on how this was done by considering the surface charge and density of interface states of the dielectric material.

## 8.2.1 Background

Passivation of a semiconductor surface is needed in order to reduce the amount of influence the surface properties has on the electrical properties of the bulk material characteristics. The termination of a periodic structure of a crystal lattice can lead to the creation of electronic states at the surface, and this leaves one or two dangling bonds per surface atom. An illustration of this is provided in Figure 8.5. These dangling bonds serve essentially as sites for chemical reactions and surface states for electronic processes. The dangling bonds can be satisfied through adsorption of water, oxygen, contaminants, or foreign atoms, but these can become sources of unwanted leakage. Otherwise, any bond that is empty will contribute to a reduction in the free energy and lowering of the energy band structure. So passivation is used in hopes to modify and control the flatband voltage, density of surface states, and leakage current.



Figure 8.5: (a)Illustration of a detector and the decreased performance due to surface leakage. (b)Illustration of the presence of dangling bonds located at the termination of the semiconductor

For detectors, the role of passivation is mainly to improve the electrical properties of the device, such as its zero bias resistance-area product  $R_0A$ . Lower  $R_0A$  values can lead to higher detectivity values, with a relationship given as:

$$D^* = \frac{\eta \lambda q}{2hc} \sqrt{\frac{R_0 A}{kT}} \tag{8.3}$$

where  $\eta$  is the internal quantum efficiency,  $\lambda$  is the wavelength, and q is the charge of an electron.

The density of surface states is one of the influences to the detector electrical performance. The interface states are unwanted because they can provide a tunneling mechanism for carriers. The states can trap a specific carrier and a charge is introduced due to accumulation or inversion at the surface. This charge can lead to band bending and Fermi-level pinning where the mid-gap states can become a source for leakage. This is particularly more difficult with longer wavelength devices because only a low amount of energy is needed to absorb or trap the carriers. The effect is higher dark current noise and trap-assisted tunneling current.

The surface charge is another influence on the performance. The charge affects the surface resistance, which has a direct contribution to the  $R_0A$  value, related as:

$$\frac{1}{R_0 A} = \frac{1}{(R_0 A)_{bulk}} + \frac{1}{r_{surface}} \frac{P}{A}$$
(8.4)

where P is the perimeter of the mesas and A is the area. Using a dielectric with customized properties, the charge of the dielectric can be used to compensate for any of charges on the surface. This will return the device to the desired flatband conditions. As mentioned earlier, the two characteristics that affect passivation are the surface charge and the interface state density. First, the surface charge will be discussed. The surface charge was found to be highly dependent on the composition of the dielectric. Details on the modification of the composition are discussed in Section 6.1.6. The flatband voltage and surface charge relationship with oxygen gas flow through the secondary assist source for SiO<sub>2</sub> is given in Figure 8.6. A higher oxygen flow rate led to a higher surface resistance and therefore, a closer-to-zero flatband voltage value. The change in the P/A plot from Figure 8.7 shows an improvement in the overall surface resistance of the device with the higher surface charge. This confirms the belief that the surface is negatively charged for long-wave devices, since a more positively charged passivation material is needed to create an overall net zero charge and less band bending. This also explains why the electrical performance was better with the SiO<sub>2</sub> passivation compared to the Si<sub>3</sub>N<sub>4</sub>, and why the opposite relationship is seen with the trend in flow rates in Figure 8.8 and Figure 8.9.

Parameters other than the flow rates were explored, and this was to verify whether other factors such as density of interface states had an influence on the detector performance. One parameter that was adjusted was the RF power in both ion sources. The power has been known to change the amount of surface damage, and this will be discussed in further detail in Section 8.4.2. The effects of the power of the secondary RF source are shown in Figure 8.10. The slope of the P/A vs.  $(R_0A)^{-1}$  line did not show any significant changes, but instead the only noticeable difference was in the uniformity of the different



Figure 8.6: The change in flatband voltage and its corresponding surface resistance with varying oxygen flow rates in the secondary source for  $SiO_2$  materials. A higher oxygen gas flux shows to lead to more positively fixed charge

sized diodes. A higher RF power was observed to remove contaminants on the surface of the sidewalls, particularly for smaller mesa dimensions. This slight removal proves the sensitivity of the device to interface states and contaminants on the surface.

Passivation of long-wave infrared detectors can become more difficult, and this may be attributed due to the sensitivity of the material superlattice. The LWIR structure typically has a higher ratio of InAs to GaSb monolayers than does the MWIR structure. This is important because InAs is approximately 85% softer than GaSb and therefore the sidewalls become more sensitive to surface damage. The ion-beam current is one parameter that can negatively impact the extent of surface damage done by the ion bombardment. Details of this are given later in this chapter. The improvements in the


Figure 8.7: Change in P/A for different  $O_2$  flow rates used in the secondary source during the SiO<sub>2</sub> deposition. The higher flow rates lowers the net surface resistance.

electrical performance of the detectors due to change in beam current are provided in the plots of Figure 8.11. The beam current is related to the surface damage, so this is the explanation for the higher slope in the P/A plot. Further, the damage can be observed in the I-V plot where the current exhibits losses due to either leakage dor tunneling around -0.2 to - 0.4 V. This behavior was no longer observed when the passivation was done with a lower beam current.

Both SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> are good materials for passivation, each with unique advantages and disadvantages. SiO<sub>2</sub> is good due to its ability to finely tune the surface charge. Si<sub>3</sub>N<sub>4</sub> has advantages due to be properties such as better thermal stability, which is important in this case since the detectors may operate as low as T = 77K, and is a more mechanically durable. Unlike SiO<sub>2</sub>, one of the disadvantages of Si<sub>3</sub>N<sub>4</sub> is more susceptibility to electron



Figure 8.8: The change in flatband voltage and its corresponding surface resistance with varying nitrogen flow rates in the secondary source for  $Si_3N_4$  materials. A higher oxygen gas flux shows to lead to more positively fixed charge

trapping in the insulator, which can lead to higher leakage currents. Therefore, one choice that may be a suitable option is  $SiO_xN_y$ , which if carefully deposited can be used to obtain the advantages of both materials. The plots of the passivation using both a  $Si_3N_4$  target with  $O_2$  assist and  $SiO_2$  target with  $N_2$  assist are given in Figure 8.12. The electrical improvements were demonstrated to be more severe for  $SiO_xN_y$  formed using the  $Si_3N_4$ with  $O_2$  assist, and it is deduced that this is due to the higher controllability with surface resistance with the  $O_2$  assist.



Figure 8.9: Change in P/A for different  $N_2$  flow rates used in the secondary source during the  $Si_3N_4$  deposition. The higher flow rates lowers the net surface resistance.

#### 8.2.3 Experimental Results for High $R_0A$ Infrared Detectors

The surface passivation of the MWIR Type-II photodetectors was performed using a single-layer SiO<sub>2</sub> dielectric layer, as shown in Figure 8.13. The SiO<sub>2</sub> films in this work were deposited using the two different techniques: PECVD and IBSD. The film thickness of the PECVD SiO<sub>2</sub> was measured to be 293.4 nm using SEM and 304.1 nm for IBSD SiO<sub>2</sub>. The PECVD system was an Oxford Plasmalab 80 Plus operated at a working pressure of 1.00 Torr with SiH<sub>4</sub> and N<sub>2</sub>O used as reactive source gases. The susceptor was heated to 160 °C and the RF source had a forward power of 20 W. The IBSD system was an Oxford IonFab 300 Plus. The working pressure of the chamber was 2.93 x  $10^{-4}$  Torr using Ar as a bombarding gas and O<sub>2</sub> as an assisted reactive gas.



Figure 8.10: Plot of the geometry dependent  $R_0A$  of the same detector passivated with  $SiO_2$  using different RF power values in the secondary RF source

was kept cooled at a temperature of 25 °C and was located 254 mm away from a 6"  $SiO_2$  target (99.99% purity). The primary deposition RF source had a forward power of 685 W and the secondary source had a forward power of 200 W. The operating conditions used for both systems were determined by a systematic optimization process involving the isolation of each system parameter(227).

The passivation was performed on Type-II InAs/GaSb superlattice photodetectors with a 50% cutoff wavelength at  $\lambda c$ , 50% ~ 4.7  $\mu m$  similar to Ref. (221). Before deposition, the samples were processed into both circular and square mesas with varying sizes ranging from 100  $\mu m$  to 400  $\mu m$  in diameter and length using standard UV photolithography and a combination of ECR-RIE and wet, citric-acid based etching. Top



Figure 8.11: (a)Geometry dependent  $(R_0A)^{-1}$  plot and (b) I-V plot of three passivated detectors with SiO<sub>2</sub> deposited using different beam currents. The dip in I-V curve occurs at negative bias vales for devices that surface damage due to the continually bombardment of the high energy ions.



Figure 8.12: Plot of P/A vs.  $(R_0A)^{-1}$  of LWIR detectors passivated with  $SiO_xN_y$  material showing the dependence on assistance source gas flow rates deposited with a (a)Si<sub>3</sub>N<sub>4</sub> target using an O<sub>2</sub> assist gas and (b)SiO<sub>2</sub> target using N<sub>2</sub> assist gas



Figure 8.13: SEM of the cross-section of a detector mesa covered with a single layer of approximately 300 nm thick  $SiO_2$ 

metal contacts of Ti/Pt/Au/Ti were deposited with electron beam evaporation. The additional thin layer of Ti was deposited on top of the Au to allow for proper adhesion of the SiO<sub>2</sub>. After metallization, the SiO<sub>2</sub> passivation layer was applied and the windows for wire bonding were opened using a diluted solution of buffered oxide etch and DI water (1:30) for the PECVD passivated samples and non-diluted solution for the IBSD passivated. Dark current-voltage measurements were performed using a Hewlett-Packard 4156A semiconductor parameter analyzer and with the sample attached to the cold finger of a liquid nitrogen cryostat operating at 80 K.

The electrical properties of the photodetectors were compared using I-V measurements, as shown in Figure 8.14. The points in the plot signify total measured current density and the curves with solid lines represent trap-assisted tunneling current density. The amount of surface leakage can be identified using trap-assisted tunneling currents, which were extracted using dark current modeling(228):

$$J_{trap} = \frac{e2m_T V M^2 N_t}{8\pi\hbar^3 (E_g - E_t)} \exp\left[-\frac{4\sqrt{2m_T (E_g - E_t)^3}}{3e\hbar F(V)}\right]$$
(8.5)

where  $m_T$  is the tunneling effective mass, V is the bias voltage,  $M2 = 1 \times 10^{-23} \text{ eV}^2\text{-cm}^3$ ,  $E_g$  is the bandgap energy,  $E_t$  is the trap energy level, and F(V) is the electric field. The fitted parameters used for the simulation were  $\tau_{GR} = 1$  ns and  $E_t = 9/10 E_g$ .



Figure 8.14: (a)Trap-assisted current densities extracted using dark-current modeling for an unpassivated, PECVD SiO<sub>2</sub> passivated, and IBSD SiO<sub>2</sub> passivated detectors. The points signify total measured current density, while the linear curves signify the modeled trap-assisted tunneling current density. (b) Plot of inverse zero-bias resistance-area product (R<sub>0</sub>A)<sup>-1</sup> relative to the perimeter to area ratio (P/A) of unpassivated, PECVD SiO<sub>2</sub> passivated, IBSD SiO<sub>2</sub> passivated photodetectors. Points were fitted to a line and the zero-bias resistance-area of the bulk material was extrapolated to 0.89 x 10<sup>6</sup>  $\Omega$ -cm<sup>2</sup> in all three cases.

For both techniques, the device electrical performance showed improvements by the  $SiO_2$  passivation. The device with PECVD  $SiO_2$  showed a 1.68 times decrease in trap

density of  $N_t = 2.5 \times 10^{13} \text{ cm}^{-2}$  compared to  $N_t = 4.2 \times 10^{13} \text{ cm}^{-2}$  for the unpassivated sample. However, a more significant improvement was seen with the IBSD SiO<sub>2</sub> sample where  $N_t = 1.1 \times 10^{11} \text{ cm}^{-2}$ . This indicates a decrease in trap density by approximately 227 times for IBSD SiO<sub>2</sub> passivated compared to the PECVD passivated sample. Further, the dark current modeling demonstrated that the IBSD SiO<sub>2</sub> passivated photodetectors were limited by generation-recombination current whereas both unpassivated and PECVD SiO<sub>2</sub> passivated detectors were limited by trap-assisted tunneling current.

The electrical properties of the photodetectors can be further compared by using the zero-bias resistance-area product  $R_0A$ , as shown in Figure 8.14. The device passivated with IBSD SiO<sub>2</sub> retained  $R_0A$  values of the same order magnitude as that of bulk material while the device passivated with PECVD SiO<sub>2</sub> led to 1-3 orders of magnitude lower  $R_0A$ . Extracted from the slope of the fitted lines, the IBSD SiO<sub>2</sub> passivated detectors had two orders of magnitude higher surface resistivity of 2.63 x 10<sup>9</sup>  $\Omega$ -cm compared to 1.38 x 10<sup>7</sup>  $\Omega$ -cm for the PECVD SiO<sub>2</sub> sample.

Finally, the last set of tests for the detectors involved ensuring the structural robustness of the passivation and its stability. If the dielectric material was not stable, then the detectors would have different performance behaviors either due to environmental factors or ageing issues. The change in  $R_0A$  for the sample is plotted with time for both the PECVD SiO<sub>2</sub> and IBSD SiO<sub>2</sub> passivated detectors, given in Figure 8.15. Both samples underwent different processes of either rinsing under water, exposure to air, pumping in vacuum and/or underfill. The stability of the device proved to be significant better with the IBSD SiO<sub>2</sub> sample. Further, another benefit with the IBSD SiO<sub>2</sub> is the ability to withstand the application of epoxy underfill without any changes in device performance or properties. This is opposite from the PECVD  $SiO_2$ , which showed failure after the application of the epoxy.



Figure 8.15: Change in  $R_0A$  for (a)PECVD SiO<sub>2</sub> and (b)IBSD SiO<sub>2</sub> passivated samples with time and different desorption/pumping processes

## 8.3 Optical Passivation

The performance of an infrared laser can be improved with lower absorption losses of the ridge insulator used to isolate the electrical metal contacts from the semiconductor waveguide. This section discusses how the ridge width can be fabricated differently for higher maximum operating temperature devices once a dielectric with lower absorption loss is used.

#### 8.3.1 Background

The internal loss of a laser has a large impact on its performance. The loss originates from many different sources and each loss has equal weighted contribution to the total:  $\alpha_i = \alpha_w + \alpha_{ridge}$ . One source of the internal loss from the insulator passivating the ridge and serving as electrical isolation between the metal contact and the active region. This becomes particularly problematic for long-wave infrared lasers that have higher losses due to the utilization of conventional insulators. For conventional insulators such as SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>, characteristic molecular vibration bands exist in specific windows, such as in the 8 - 12  $\mu$ m wavelength range. Since absorption bands are characteristic to the materials, the only way to avoid this issue is to use alternative materials. However, there currently a good alternative material has not been sought. This section discusses how a different material was chosen and solutions to overcoming any necessary issues are presented.

The current solution to minimizing the ridge insulator loss is to fabricate the lasers with wider ridges. The reason why this alleviates the problem is shown with the illustration of a ridge waveguide and field penetration given in Figure 8.16. It can be observed that the first order lateral mode extends further out than the fundamental mode, and as a result, losses outside of the ridge have a greater affect on the first order mode(229). The reason why wider ridges is a solution is because then there exists a a larger gap between the evanescent tail of the first order and fundamental mode. The results of this is that losses become more selectively introduced to the first order mode. While widening of the ridge will reduce the amount of loss coupled to the fundamental mode, one problem is that wider

ridges lead to a lower amount of heat dissipated. This is shown in Figure 8.16 where, for lasers operating at higher duty cycles, the benefits of a lower ridge insulator loss may be masked by the performance degradation due to the higher amount of internal heating. This limits the improvements attained by the fabrication of wider ridges, especially for lasers operating at higher temperatures or higher duty cycles.



Figure 8.16: Illustration of the (a) fundamental and first order lateral mode for a laser with a wide ridge width and (b) poor heat dissipation due to fabrication of wider ridges

In order to quantify the improvements in loss due to the change in insulator loss  $\alpha_{ins}$ , insulator thickness d, and ridge width w, the ridge loss relationship is given by:

$$\alpha_{ridge} \approx \alpha_{ins} \left[ \frac{d}{w+2d} - \frac{1}{\pi} \sin(\frac{\pi w}{w+2d}) \right]$$
(8.6)

Figure 8.17 plots the ridge insulator loss calculated as a function of different insulator thicknesses for three different materials. As can be observed, all materials exhibited a lower loss when the ridge width was wider. Typically, a thickness around 400 nm is used, which leads to a difference in loss is up to  $0.5 \text{ cm}^{-1}$ . The impact of the less absorbing insulator becomes more apparent when the ridge width is reduced, with a difference in

ridge loss greater than  $1.5 \text{ cm}^{-1}$ . Therefore utilization of an insulator with less absorbing dielectrics, such as  $Y_2O_3$ , is essential.



Figure 8.17: Ridge loss versus insulator thickness for three different dielectrics with a (a) 13  $\mu$ m ridge width and (b) 20  $\mu$ m ridge width

#### 8.3.2 Material Selection and Design

The choice of material to use for the ridge insulator is mainly dependent on the absorption losses in the long wavelength regions. The absorption coefficient plots of five materials are shown in Figure 8.18. For a targeted wavelength 8.8  $\mu$ m, ZnO has the lowest absorption coefficient with the amount of absorption in Y<sub>2</sub>O<sub>3</sub> not being significantly more. However, ZnO cannot be used because of its conductive nature. It will causes problem with forming a conduction path between the laser itself and the metal contacts.

In addition to low absorption coefficient, there are other properties necessary for this application. First, the material must not have pinholes. The reason is because an elec-



Figure 8.18: Absorption loss for five different insulators showing the difference in the 8 - 12  $\mu {\rm m}$  range

trolyte solution is used for electroplating a thick gold layer as the metal contact, and it is undesirable to have the semiconductor not protected from the solution. Another property is high dielectric breakdown strengths. The reason why this is important is because the dielectric must be robust enough and not breakdown during laser operation. This includes durability in operating conditions that involves high electric fields and high operating temperatures. Achieving high dielectric breakdown strengths have been shown to be related to the material density in Section 7.7.2. Finally, the last important quality is to have a material that can be etched, and this is necessary for the metal contact opening. The ridge width can vary significantly from 6 - 25  $\mu$ m, and with a 3 - 5  $\mu$ m opening, it is desirable to have as little undercut or overhang. As discussed earlier, Y<sub>2</sub>O<sub>3</sub> is a good choice for an insulator, but it does pose difficulties with the etching process.



Figure 8.19: Side profile of  $Y_2O_3$  etched with (a) $H_3PO_4$  based chemical acid, and (b)Ar +  $Cl_2$  based dry etch without utilization of optimized power values.

During etching of  $Y_2O_3$ , an issue with the sidewall profile was discovered. The sidewalls exhibited a jagged shape as shown in Figure 8.19. This is due to the difference in etching from the Ar and from the Cl<sub>2</sub> bonds. It was experimentally discovered that the jagged shape can be modified mainly by adjusting the RF power. The changes are shown in Figure 8.20, where a significant change is shown when reducing the power from 300 W to 200 W and then again to 100 W. Using an RF power value of 100 W, an etch rate around 8 - 9 nm/min should be expected.



Figure 8.20: SEM graphs of the sidewalls of dry etched  $Y_2O_3$  show degree of jagged characteristics using RF powers of (a) 300 W, (b) 200 W, and (c) 100 W

Once the jagged sidewall issue was resolved, the last final step was to clean up any remaining residue, which is shown after the photoresist has been removed in Figure 8.21. The residue was removed by exposing the sample to a post-process chemical dip in a solution consisting of 20:3:1:10 of  $H_3PO_4$ :HNO<sub>3</sub>:CH<sub>3</sub>COOH:H<sub>2</sub>O. This dip was done for 1-2 seconds and controllability is best achieved when the mixture is cooled down to a temperature of 15 °C.



Figure 8.21: SEM cross-section of dry etched  $Y_2O_3$  without and with a post-process chemical dip in cooled 20:3:1:10  $H_3PO_4$ :HNO<sub>3</sub>:CH<sub>3</sub>COOH:H<sub>2</sub>O mixture

# 8.3.3 Experimental Predictions for High Max Operating Temperature Infrared Lasers

The lasers were fabricated with ridge widths of around 20  $\mu$ m with deposited thickness values of around 400 nm. The exact values measured by SEM were found to be W = 20.4 m with 437 nm SiO<sub>2</sub>, W = 18.9  $\mu$ m with 467 nm Si<sub>3</sub>N<sub>4</sub>, and W = 19.0  $\mu$ m with 442 nm Y<sub>2</sub>O<sub>3</sub>. The P-I-V curves of the three lasers are given in Figure 8.22. The graph shows three different threshold current density values of  $J^{th}_{SiO2} = 4.85 \text{ kA/cm}^2$ ,  $J^{th}_{Si3N4} = 3.41 \text{ kA/cm}^2$ , and  $J^{th}_{Y2O3} = 2.05 \text{ kA/cm}^2$  and three different slope efficiency values  $\eta_{s}|_{SiO2} = 218 \text{ mW/A}$ ,  $\eta_{s}|_{Si3N4} = 236 \text{ mW/A}$ , and  $\eta_{s}|_{Y2O3} = 368 \text{ mW/A}$ . Demonstrated on another laser with better performance, it is predicted that the optical passivation will lead up to 47% improvement in  $J_{th}$  and about 2.5 times improvement in the slope efficiency.

This comparison works well in achieving high output power by reducing the internal loss, but another way to use this technique is by fabricating the laser with the same ridge loss. Since the loss from the insulator is lower, the same ridge loss is attained by using a more narrow ridge width for better thermal management. A plot demonstrating the large difference in thermal heatsinking for the same laser fabricated with two different ridge widths is observed in Figure 8.23. The performance improvement predictions are over two times higher maximum operating duty cycle and up to 24% higher maximum operating temperature.

## 8.4 Experimental Challenges

There were three main challenges faced when working with the materials and devices in this chapter. This includes surface adhesion, surface oxidation, and surface damage. Solutions to these issues have been found and will be provided in this section.



Figure 8.22: P-I-V curves of a 20  $\mu$ m fabricated laser with three different ridge insulators of thickness of about 430 nm

#### 8.4.1 Surface Adhesion

The success of a film adhering to a surface or substrate is dependent on the surface energy values of the film  $\gamma_f$ , surface or substrate  $\gamma_s$ , and interface  $\gamma_{fs}$ . This is illustrated in Figure 8.24. The work required to separate the area is given as  $W_A = \gamma_f + \gamma_s - \gamma_{fs}$ . If  $W_A > 0$ , then this represents the strength for adhesion and if  $W_A < 0$  then this denotes the strength for repulsion.

As discussed in Section 6.1.2, adhesion of the film typically occurs when the surface is compressively stressed. An example sample with poor adhesion is shown in Figure 8.25. The film demonstrates good adhesion to itself instead of good adhesion to the surface. This means that the energy at the interface is greater than both the energy of the film



Figure 8.23: Average power values for different duty cycles of the same laser with same ridge insulator fabricated with two different ridge widths. The plot exhibits the significant difference in thermal management due to the ridge.



Figure 8.24: Illustration showing the surface energies of a film on substrate

and the energy at the substrate. The surface energy plays such a significant role because it determines whether the dielectric atoms will become more tightly bound to each other. One way to overcome this is by deposition at higher energy values, higher RF powers, and low substrate-to-target angle. The secondary ion-assistance source can play a large role also. This includes not only higher RF powers, but this also means lower gas flux.



Figure 8.25: SEM pictures of internal stress in films demonstrating compressive stress where the film has enough energy adhere to itself, but does poorly in adhering to the substrate

The higher energy will promote a mixing or adhesion between atoms that would not do so if the secondary source were not used.

In addition to adjustment of the parameters, there can be a number of alternatives for for enhancement the adhesion of a material. The first is with a pre-cleaning process, as detailed in Section 2.2.2. Cleaning of the substrate prior to the deposition will help to remove contaminants and can also rearrange atoms for more favorable adhesion. Another method to promote adhesion is with ion-beam stitching. The idea here is similar to the second method, but instead the beam in the secondary source is used instead of just the plasma. This end result can be observed in Figure 8.26. The adhesion of ZnSe is poor to ZnO material, but this can be improved by "stitching" the material together. Additionally, the material can also be annealed to reduce the interfacial energy, as discussed in Section 6.2.2. The last solution is the utilization of an adhesive layer. The adhesive layer can be used in situations where the interfacial energy of a film to substrate is too high, but the



interfacial energy of the adhesive layer to both the film and substrate is not.

Figure 8.26: SEM graphs of ZnSe on Si substrate before and after ZnO deposition. The ZnO was deposited using the ion-beam stitching technique to promote adhesion

To be able to relatively compare the adhesion of a film is very important. One way in doing so is by using either the tape test or scratch test. The results of scratch tests viewed under optical microscope for two different samples using the same load and stylus radius is shown in Figure 8.27. It is concluded that ZnSe has a lower  $W_A$  value than SiO<sub>2</sub> due to the wider scratch revealed under the microscope. A higher adhesion force means better adhesion between the film and substrate, and the force is inversely proportional to the width b of the scratch and R radius of the stylus(230).

#### 8.4.2 Surface Damage From Ion Bombardment

One disadvantage of the IBSD system that often times leads to performance degradation is the amount of surface damage due to continual bombardment of the high energy ions. The surface damage can lead to unwanted effects such as interfacial mixing or the introduction



Figure 8.27: Scratch test demonstrated on 100 nm thick ZnSe and SiO<sub>2</sub> on GaSb. The width scratch observed with the ZnSe shows how it does not have as good adhesion as  $SiO_2$ 

of unwanted surface states. Both have been shown to demonstrate issues with device performance. Relative comparison of the amount of surface damage can be done by observing the magnitude of the PL intensity of the substrate peak, as shown in Figure 8.28. Any reduction in intensity is an indication of a higher amount of surface damage. In the plot, the SiO<sub>2</sub> sample #2 exhibited a lower density than SiO<sub>2</sub> sample #1. While it is ideal to have no induced surface damage, this becomes an extremely complicated problem for systems utilizing plasmas and is one of the disadvantages to the IBSD system

There are many different ways to reduce the amount of surface damage from the ion bombardment. One way to do so is by using a lighter sputtering gas such as helium or xenon. The idea is to use a mass that is lighter than argon, and therefore leads to a lower amount of momentum transfer. A disadvantage to using this option is that the sputtering yield will be lower and therefore longer deposition times should be expected. Another factor that can be adjusted for is the ratio of the deposition rate to plasma



Figure 8.28: Reduction in PL intensity observed due to non-radiative recombination through creation of surface states due to ion induced damage

power. A higher ratio will lead to a higher amount of surface damage. Similar to the previously discussed alternative, this will lead to long deposition times. Finally, the main contributor to surface damage was found to be the energetic argon atoms. The severity of the damage caused by the atoms depends on many factors like energy, acceleration, and charge. The energy can be adjusted with the beam current or beam voltage in the primary source. The acceleration can be dealt with by considering the amount of target charging and the potential difference between the target and substrate. By keeping the both the target backing plate and substrate holder grounded, this reduces the amount of charge induced on the target and also reduces the amount of acceleration the atom undergoes in transport. Finally, the charge is extremely important. It has been found by Ref. (11) that the highest amount of damage occurs for neutrally charged atoms, so the extent can be reduced by negative ionization of the atoms prior to reaching the substrate. However, it was shown that the presence of negative  $O^-$  ions does not contribute to the surface damage.

### 8.5 Summary

This chapter discussed surface passivation by approaching it from three different perspectives. Objectives were based on improving the isolated structural, electrical, or optical properties of the dielectrics. With tuning of the material characteristics, it is hypothesized that each unique issue can be alleviated with the limitation being targeted specifically. Improvement in the structural properties involved achieving higher damage threshold for high output power density lasers. This was done by designing the HR coating structure to use materials with low absorption and low interfacial states and appropriately redistributing the electric field intensity to coincide the maximum values to lie in areas of high resistance. Once the structure was redesigned, the objective of having a structurally robust laser was satisfied. Improvement in the electrical properties involved using a dielectric material to change the surface charge and density of interface states of a detector to achieve close-to-bulk  $R_0A$  values. The role of the surface charge and interface states is to prevent band bending and therefore lower the loss due to high leakage currents. Finally, the last improvement was done by lowering the absorption loss of the ridge insulator passivating a laser waveguide. With a lower absorption loss, the internal loss of the laser is expected to become lower and so there is more tolerance for the fabrication of narrower

ridge widths and higher maximum operating temperature. Finally, solutions were given to three of the major experimental challenges that were faced. These challenges included surface damage from the higher energy ions, surface oxidation, and poor adhesion of the film to the substrate.

# **CHAPTER 9**

# Future Work

Chapter 2 through Chapter 6 provided the background necessary to apply and effectively use the IBSD system and seven different dielectric materials for the two applications discussed in detail: optical coatings and surface passivation. Now that the necessary work has been done to optimize, characterize, and fully understand the properties and behavior of the films, the remaining future work involves applying these films to other applications and achieving overall device improvements. Both infrared lasers and detectors can have a diverse range of applications, and therefore the performance objectives can vary significantly. This can lead to different requirements in terms of the thin-film growth conditions and properties, and there can be a number of different future projects done with these devices and the physical background provided in this work. However to also explore other types of devices, this section provides the background for UV devices.

# 9.1 Lateral Epitaxial Overgrowth

The quality of the dielectric mask is important in affecting the formation of dislocations in the crystalline grown material. The dislocations can be observed as shown in Figure 8 1, and a large density is unwanted as the dislocations typically lead to deterioration in the optical and electrical performance of the device.



Figure 9.1: SEM and optical microscope figures of the dielectric mask and the epitaxially overgrown material showing the pattern, fill factor, and dislocation density

The quality and structure of the dielectric mask has many different ways in enhancing the formation of dislocations in the overgrown material. The largest influence of the material quality is due to the density of defects or impurities. The impurities in the mask will propagate to the top surface and serve as a poor template for the overgrowth. Minimization of the defect density and impurities can be done using many techniques similar to those given in Section 6.1.4(231). Finally, one last consideration in addition to material quality is the structure and pattern of the dielectric mask. It has been reported by Ref. (231) and (232) that the fill factor of the mask is important, where a higher fill factor was found to lead to lower dislocation densities due to the influence in reactant diffusion length.

## 9.2 UV Light Emitting Diodes and Optical Sensors

Optical sensors and light emitting diodes using ZnO have received much attention lately as methodology for selective gas detection(103). ZnO has been found to be a good transparent conducting oxide TCO film due to its large bandgap, high conductivity and stability. Similar to TiO2, ZnO has advantages over other materials in the ability to modify the photocatalytic activity. There are other techniques that are used for deposition of ZnObased optical sensors and LEDs, such as PLD. However, there are many advantages and disadvantages to PLD, and therefore this section discusses the potential in using IBSD as an alternative.

To properly fabricate a UV LED using a ZnO TCO, the material needs to be doped p-type. ZnO grows naturally as n-type, so impurities must be introduced to achieve this. The initial attempt with p-type doping of ZnO was done using N2 assist during the deposition process with the highest substrate temperature possible and the lowest deposition rate. However, it was only until after annealing in N2 gas at 1000 °C for 1 minute, that the material exhibited p-type characteristics. The proof of p-type doping was exhibited in changes in PL spectra over a span of two days when the sample was not handled. This is shown in Figure 9.2. Further, it was confirmed the formation of a device due through electroluminescence spectra. This work presented here was initial attempts in both doping and fabrication of a UV LED using IBSD ZnO as the TCO. Further work can be done in both optimizing the doping and crystalline quality and development of the fabrication for the LED. It has to be noted that the choice of substrate is extraordinarily important in the crystalline quality of the material, where the most success was found to occur when using high quality GaN, Al2O3, or GaAs, similar to Ref. (233).



Figure 9.2: Change in PL spectra of the same p-type doped ZnO sample measured over two different days

Gold nanoclusters can be used to coat thin ZnO nanostructures for applications such as gas detection of butane with expected improved sensitivity(234)(235). The gold nanoclusters can be formed by deposition of gold on top of substrate followed by ZnO on top of the gold. An initial attempt shows nice formation of the nanoclusters given in the SEM picture of Figure 9.3. The formation of the nanoclusters was done by first depositing 15 nm of gold onto silicon substrate. The sample was then annealed for 1 minute at 900 °C and finally, 350 nm of ZnO was deposited on top. A post-ZnO deposition annealing step led to observed improvements in the PL intensity similar to Figure 6.11.



Figure 9.3: Gold nanoclusters formed with 15 nm Au deposited on Si substrate followed by 900 C rapid thermal anneal and 350 nm ZnO deposition.

The proper sequence for formation of Au-clustered ZnO has been developed. The PL exhibited recombination behavior as expected, so further characterization such as transmission measurements may prove to be necessary. Future work involves fabrication of this into an actual device and testing for the appropriate gas detection.

## 9.3 UV Solar Cells

The development of UV solar cells has become a large research interest and their advancement can be aided by the dielectric material quality from the IBSD system. The material would serve as a contact or electrode and objectives would be to have a material with both high conductivity and good transparency. Two suitable materials include ZnO and TiO2, and a brief discussion will be provided in this section. Zinc oxide is a good transparent contact for solar cells with enhanced transparency and conductivity when Al or Au-doped. They can be particularly used for front contacts on silicon thin film solar cells because of being efficient with light trapping(236).

TiO2 is a good material to be used for dye-sensitized solar cells, and it is a suitable choice due to its light absorption and high photoelectrical response. It also has other desirable properties including large surface area, enhanced absorption of light, good adhesion, and high conductivity(237).

One very important merit for solar cells is the photoelectric conversion efficiency, which is the ratio of the output power to the incident power.

$$\eta = \frac{J_{sc}V_{OC}FF}{Pin} \tag{9.1}$$

where  $J_{sc}$  is the short circuit current divided by the area of the cell,  $V_{OC}$  is the open circuit voltage, FF is the fill factor, and Pin is the intensity of incident light. So any change in material property to achieve a high efficiency value is desired. Particularly,  $J_{sc}$ is a key parameter to determining the efficiency where a high value means there is an enhanced number of photo generated electrons transferred to the electrodes. Two factors that affect  $J_{sc}$  are the grain size and void volume of the material. Both larger grain sizes are large void volumes will lead to higher values, and this can be achieved by developing more porous films. Details on how to work with the sputtering parameters to achieve porous materials can be found in Section 6.1.1.

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## APPENDIX A

#### Characterization and Optimization Tables

Tables of the optimization process including the characterization results are given here. This information was used for the spatial parameter mapping of Chapter 5. The information provided is not an extensive list of the deposition parameters and characterization results that can be explored, since only the information necessary for this work was extracted.

#### A.1 PbTe

	Ι		Deposit	tion Source			Assist Source			Substrate	
No.	Press.	Ion	Ion	Ar	$O_2$	$\mathbf{RF}$	Ar	$N_2$	$\mathbf{RF}$	Temp	Angle
		Beam	Beam	Gas	$\operatorname{Gas}$	Power	$\operatorname{Gas}$	$\operatorname{Gas}$	Power		
300	0.62	70	600	5	0	556	0	0	0	30	25
301	0.62	74	600	5	0	569	0	0	0	30	25
302	0.62	77	600	5	0	585	0	0	0	30	25
303	0.62	82	600	5	0	643	0	0	0	30	25
304	0.62	86	600	5	0	671	0	0	0	30	25
305	0.62	82	500	5	0	606	0	0	0	30	25
306	0.62	82	550	5	0	658	0	0	0	30	25
307	0.62	82	650	5	0	513	0	0	0	30	25
308	0.62	82	700	5	0	503	0	0	0	30	25
309	0.62	82	600	9	0	535	0	0	0	30	25
310	0.62	82	600	13	0	494	0	0	0	30	25
311	0.62	82	600	17	0	451	0	0	0	30	25
312	0.62	82	600	20	0	449	0	0	0	30	25
313	0.62	82	600	5	0	686	0	0	0	30	15
314	0.62	82	600	5	0	673	0	0	0	30	20
315	0.62	82	600	5	0	682	0	0	0	30	30
316	0.62	82	600	5	0	685	0	0	0	30	35
317	0.62	82	600	5	0	699	0	0	0	110	25
318	0.62	82	600	5	0	708	0	0	0	190	25
319	0.62	82	600	5	0	694	0	0	0	270	25
320	0.62	82	600	5	0	704	0	0	0	350	25
341	0.62	82	600	5	0	702	0	0	200	30	25
342	0.62	82	600	5	0	700	0	0	300	30	25
343	0.62	82	600	5	0	699	0	0	400	30	25
344	0.62	82	600	5	0	698	0	0	500	30	25
345	0.62	82	600	5	0	703	0	0	600	30	25
375	0.62	82	600	5	0	704	0	20	300	30	25
376	0.62	82	600	5	0	699	0	15	300	30	25
377	0.62	82	600	5	0	683	0	10	300	30	25
378	0.62	82	600	5	0	688	0	5	300	30	25
379	0.62	82	600	5	0	685	0	0	300	30	25
380	0.62	82	600	5	0	702	5	0	300	30	25

Table A.1: Table of optimization conditions for PbTe

No.	Deposition	Refractive	Absorption	AFM
	Rate	Index	Coefficient	Roughness
	[nm/sec]		$[\mathrm{cm}^{-1}]$	[nm]
300	8.08	4.75	450.13	1.540
301	8.12	4.75	452.92	1.173
302	8.92	4.76	562.01	2.259
303	9.93	4.76	302.19	1.932
304	12.33	4.76	287.20	1.533
305	6.42	4.74	281.03	1.134
306	7.83	4.75	298.19	1.214
307	9.75	4.76	350.21	2.108
308	10.31	4.75	405.20	2.221
309	5.92	4.72	204.19	1.055
310	5.01	4.74	299.29	1.071
311	4.83	4.78	350.29	1.182
312	4.83	4.77	489.93	1.401
313	6.20	4.78	520.19	2.032
314	5.42	4.77	492.81	1.996
315	5.22	4.77	334.59	0.614
316	6.22	4.77	259.29	0.440
317	7.25	4.77	501.90	2.795
318	7.23	4.78	590.39	4.112
319	7.15	4.78	620.33	5.893
320	7.15	4.78	788.67	5.893
341	4.56	4.76	601.02	3.537
342	5.10	4.76	567.10	2.493
343	6.60	4.74	350.55	1.019
344	7.12	4.74	360.21	1.928
345	7.93	4.74	401.39	2.093
375	8.29	4.70	560.21	4.192
376	7.29	4.71	501.39	3.201
377	7.20	4.72	436.10	2.392
378	6.72	4.73	335.10	2.001
379	6.01	4.74	367.02	2.109
380	5.20	4.88	676.01	4.209

Table A.2: Characterization results from PbTe optimization process

## $\mathbf{A.2} \quad \mathbf{SiO}_2$

	Deposition Source			Source	Assist Source			Substrate			
No.	Press.	Ion	Ion	$\operatorname{Ar}$	$O_2$	$\mathbf{RF}$	Ar	$N_2$	$\operatorname{RF}$	Temp	Angle
		Beam	Beam	Gas	Gas	Power	Gas	Gas	Power		
	$10^{-4}$	Curr.	Volt.	Flow	Flow		Flow	Flow			
	[Torr]	[mA]	[V]	[sccm]	[sccm]	[W]	[sccm]	[sccm]	[W]	$[^{\circ}C]$	[°]
88	1.91	130	750	5	0	766	0	10	0	30	25
89	1.91	130	750	5	0	786	0	10	0	30	30
90	1.91	130	750	5	0	771	0	10	0	30	35
91	1.91	130	750	5	0	816	0	10	0	30	20
92	1.91	130	750	5	0	773	0	10	0	30	15
183	1.05	130	750	5	1	585	3	0	600	30	25
184	1.27	130	750	5	1	599	3	2.5	600	30	25
185	1.70	130	750	5	1	600	3	7	600	30	25
186	2.93	130	750	5	1	603	3	17.7	600	30	25
187	3.14	130	750	5	1	575	3	20	600	30	25
193	3.34	148	750	5	1	669	3	17.7	600	30	25
194	3.94	170	750	5	1	853	3	17.7	600	30	25
195	2.93	108	750	5	1	470	3	17.7	600	30	25
196	2.14	86	750	5	1	385	3	17.7	600	30	25
197	2.73	170	800	5	1	811	3	17.7	600	30	25
198	2.73	170	875	5	1	751	3	17.7	600	30	25
199	2.73	170	925	5	1	764	3	17.7	600	30	25
200	2.73	170	1000	5	1	716	3	17.7	600	30	25
203	1.05	108	1000	5	0	484	0	4	600	30	25
204	0.62	108	1000	5	0	473	5	4	600	30	25
205	1.07	108	1000	9	0	475	0	4	600	30	25
206	1.49	108	1000	13	0	473	0	4	600	30	25
207	2.14	108	1000	17	0	472	0	4	600	30	25
208	0.62	108	1000	5	0	470	0	4	600	110	25
209	0.62	108	1000	5	0	470	0	4	600	190	25
210	0.62	108	1000	5	0	482	0	4	600	270	25
211	0.62	108	1000	5	0	481	0	4	600	350	25
212	1.05	108	1000	5	5	505	0	4	600	30	25
213	0.62	108	1000	5	0	479	0	4	400	30	25
214	0.62	108	1000	5	0	478	0	4	500	30	25
215	0.62	108	1000	5	0	489	0	4	700	30	25
216	0.62	108	1000	5	0	479	0	4	300	30	25

Table A.3: Table of optimization conditions for  $SiO_2$ 

No.	Deposition	Refractive	Absorption	AFM	Etch
	Rate	Index	Coefficient	Roughness	Rate
	[nm/sec]		$[\mathrm{cm}^{-1}]$	[nm]	
88	2.97	1.47	459.68	0.643	2.25
89	3.26	1.47	497.88	1.563	3.54
90	4.50	1.46	589.87	5.482	4.01
91	2.45	1.46	623.79	1.272	1.90
92	2.36	1.46	635.1	3.910	1.75
183	4.11	1.37	79.59	0.234	13.14
184	3.72	1.49	105.03	0.205	8.20
185	3.50	1.59	121.47	0.176	3.69
186	3.21	1.50	98.72	0.149	2.14
187	3.45	1.33	79.94	0.305	5.90
193	3.43	1.25	54.45	0.167	2.46
194	3.24	1.40	51.31	0.222	3.06
195	2.60	1.54	70.16	0.129	2.39
196	1.91	1.79	150.80	0.140	3.07
197	3.49	1.20	65.62	0.163	2.76
198	4.38	1.24	61.78	0.334	2.36
199	4.65	1.46	87.27	0.177	1.79
200	4.67	1.60	111.70	0.245	1.40
203	4.10	1.38	80.63	0.179	4.10
204	3.71	1.43	1016.33	0.195	2.99
205	3.74	1.47	238.76	0.186	3.74
206	3.71	1.51	211.37	0.169	3.71
207	3.89	1.47	552.92	0.148	3.89
208	3.69	1.63	126.36	0.197	3.69
209	3.65	1.60	157.14	0.123	2.25
210	3.64	1.52	162.67	0.546	1.97
211	3.63	1.44	108.56	0.116	2.92
212	4.75	1.42	956.73	0.466	8.46
213	3.89	1.37	59.34	1.015	3.38
214	4.05	1.42	69.81	0.133	3.57
215	3.73	1.40	86.22	0.135	3.61
216	3.72	1.26	111.00	0.162	2.97

Table A.4: Characterization results from  $SiO_2$  optimization process

# A.3 $Si_3N_4$

				Deposition Source			Ass	sist Sou	rce	Substrate	
No.	Press.	Ion	Ion	Ar	$O_2$	$\mathbf{RF}$	Ar	$N_2$	$\mathbf{RF}$	Temp	Angle
		Beam	Beam	Gas	Gas	Power	Gas	Gas	Power		
	$10^{-4}$	Curr.	Volt.	Flow	Flow		Flow	Flow			
	[Torr]	[mA]	[V]	[sccm]	[sccm]	[W]	[sccm]	[sccm]	[W]	$[^{\circ}C]$	[°]
476	1.49	100	750	5	0	652	0	5	400	350	25
477	1.49	100	750	5	0	654	0	5	400	30	25
478	1.49	100	750	5	0	665	0	5	400	110	25
479	1.49	100	750	5	0	665	0	5	400	190	25
480	1.49	100	750	5	0	670	0	5	400	270	25
481	2.43	86	750	5	0	521	0	5	400	30	25
482	2.11	86	800	5	0	536	0	5	400	30	25
483	1.93	86	875	5	0	519	0	5	400	30	25
484	1.70	86	925	5	0	511	0	5	400	30	25
485	1.49	86	1000	5	0	504	0	5	400	30	25
486	1.27	108	875	5	0	658	0	5	400	110	25
487	1.05	130	875	5	0	705	0	5	400	110	25
488	0.82	148	875	5	0	743	0	5	400	110	25
489	0.62	170	875	5	0	811	0	5	400	110	25
490	1.93	86	875	5	0	531	0	5	200	30	25
491	1.93	86	875	5	0	523	0	5	300	30	25
492	1.93	86	875	5	0	530	0	5	500	30	25
493	1.93	86	875	5	0	535	0	5	600	30	25
494	1.70	86	875	0	0	542	0	5	200	30	25
495	2.11	86	875	10	0	531	0	5	200	30	25
496	2.43	86	875	15	0	528	0	5	200	30	25
497	3.11	86	875	20	0	539	0	5	200	30	25
498	2.43	85	875	5	0	542	5	5	200	30	25
499	1.93	86	875	5	0	556	0	0	200	30	25
500	2.43	86	875	5	0	554	0	10	200	30	25
501	3.34	86	875	5	0	562	0	15	200	30	25
502	4.43	86	875	5	0	558	0	20	200	30	25
503	1.93	86	875	5	0	533	0	5	200	30	15
504	1.93	86	875	5	0	525	0	5	200	30	20
505	1.93	86	875	5	0	528	0	5	200	30	30
506	1.93	86	875	5	0	543	0	5	200	30	35

Table A.5: Table of optimization conditions for  $\rm Si_3N_4$ 

No.	Deposition	Refractive	Absorption	AFM
	Rate	Index	Coefficient	Roughness
	[nm/sec]		$[\mathrm{cm}^{-1}]$	[nm]
476	3.76	2.05	820.10	0.110
477	4.55	2.05	652.03	0.135
478	4.29	2.04	720.92	0.145
479	4.01	2.05	798.22	0.166
480	3.92	2.04	810.01	0.179
481	3.56	2.04	692.91	0.143
482	3.91	2.02	725.93	0.159
483	4.01	2.03	773.29	0.198
484	4.27	2.04	791.20	0.210
485	4.58	2.03	830.21	0.221
486	4.35	2.03	720.39	0.198
487	4.67	2.03	790.20	0.189
488	4.82	2.03	823.41	0.197
489	5.00	2.04	855.67	0.192
490	3.21	2.04	655.90	0.201
491	3.76	2.04	728.33	0.165
492	4.10	2.04	901.90	0.169
493	4.33	2.05	1029.32	0.172
494	4.29	2.05	840.20	0.183
495	4.10	2.03	749.52	0.198
496	4.12	2.03	923.20	0.210
497	4.98	2.02	810.22	0.201
498	3.21	2.03	1105.21	0.179
499	5.10	2.04	727.23	0.188
500	4.82	2.03	765.29	0.192
501	4.51	2.03	849.91	0.321
502	4.20	2.03	933.21	0.339
503	3.98	2.02	873.98	0.201
504	3.18	2.02	782.92	0.223
505	3.22	2.05	729.29	0.284
506	3.52	2.05	882.11	0.291

Table A.6: Characterization results from  $\mathrm{Si}_3\mathrm{N}_4$  optimization process

# A.4 $TiO_2$

	Deposition So			Source	Assist Source			rce	Substrate		
No.	Press.	Ion	Ion	Ar	$O_2$	$\mathbf{RF}$	Ar	$N_2$	$\mathbf{RF}$	Temp	Angle
		Beam	Beam	Gas	Gas	Power	Gas	Gas	Power	-	
	$10^{-4}$	Curr.	Volt.	Flow	Flow		Flow	Flow			
	[Torr]	[mA]	[V]	[sccm]	$[\operatorname{sccm}]$	[W]	[sccm]	$[\operatorname{sccm}]$	[W]	$[^{\circ}C]$	[°]
83	1.70	130	750	5	1	683	5	5	600	30	25
84	1.05	108	750	5	1	556	5	5	600	30	25
85	0.82	86	750	5	1	463	5	5	600	30	25
86	2.93	170	750	5	1	811	5	5	600	30	25
87	2.34	148	750	5	1	758	5	5	600	30	25
94	1.21	130	800	5	1	611	5	5	600	30	25
95	1.05	130	875	5	1	586	5	5	600	30	25
96	0.82	130	925	5	1	535	5	5	600	30	25
97	0.62	130	1000	5	1	462	5	5	600	30	25
98	2.34	130	750	13	1	680	5	5	600	30	25
99	1.91	130	750	7	1	673	5	5	600	30	25
100	1.21	130	750	3	1	682	5	5	600	30	25
101	3.34	130	750	20	1	685	5	5	600	30	25
102	1.70	130	750	5	1	838	5	5	500	30	25
103	1.70	130	750	5	1	841	5	5	700	30	25
104	1.70	130	750	5	1	842	5	5	400	30	25
105	1.70	130	750	5	1	845	5	5	300	30	25
106	1.05	130	750	5	1	853	0	5	600	30	25
107	1.93	130	750	5	1	847	10	5	600	30	25
108	2.11	130	750	5	1	848	15	5	600	30	25
109	3.34	130	750	5	1	848	20	5	600	30	25
110	1.70	130	750	5	1	852	5	5	600	110	25
111	1.70	130	750	5	1	850	5	5	600	190	25
112	1.70	130	750	5	1	851	5	5	600	270	25
113	1.70	130	750	5	1	848	5	5	600	350	25
115	1.70	130	750	5	1	838	5	5	600	30	20
116	1.70	130	750	5	1	839	5	5	600	30	30
117	1.70	130	750	5	1	842	5	5	600	30	35
163	1.70	130	750	5	1	844	5	5	600	30	25
165	1.21	130	750	5	1	833	5	0	600	30	25
166	2.11	130	750	5	1	833	5	10	600	30	25
167	3.43	130	750	5	1	832	5	15	600	30	25
168	4.34	130	750	5	1	830	5	20	600	30	25

Table A.7: Table of optimization conditions for  ${\rm TiO_2}$ 

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	No.	Deposition	Refractive	Absorption	AFM
$\begin{array}{                                    $		Rate	Index	Coefficient	Roughness
83 $2.11$ $2.25$ $823.65$ $6.001$ $84$ $1.70$ $2.22$ $880.50$ $5.577$ $85$ $1.60$ $2.16$ $1096.10$ $8.230$ $86$ $2.20$ $2.20$ $854.30$ $4.080$ $87$ $2.13$ $2.26$ $701.20$ $2.560$ $93$ $2.16$ $2.12$ $1028.72$ $3.991$ $94$ $2.25$ $2.12$ $1024.20$ $3.482$ $95$ $2.56$ $2.22$ $832.30$ $3.209$ $96$ $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ <td></td> <td>[nm/sec]</td> <td></td> <td><math>[\mathrm{cm}^{-1}]</math></td> <td>[nm]</td>		[nm/sec]		$[\mathrm{cm}^{-1}]$	[nm]
84 $1.70$ $2.22$ $880.50$ $5.577$ $85$ $1.60$ $2.16$ $1096.10$ $8.230$ $86$ $2.20$ $2.20$ $854.30$ $4.080$ $87$ $2.13$ $2.26$ $701.20$ $2.560$ $93$ $2.16$ $2.12$ $1028.72$ $3.991$ $94$ $2.25$ $2.12$ $1024.20$ $3.482$ $95$ $2.56$ $2.22$ $832.30$ $3.209$ $96$ $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1095.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$	83	2.11	2.25	823.65	6.001
851.602.161096.108.230 $86$ 2.202.20 $854.30$ $4.080$ $87$ 2.132.26 $701.20$ $2.560$ $93$ 2.162.12 $1028.72$ $3.991$ $94$ 2.252.12 $1024.20$ $3.482$ $95$ 2.562.22 $832.30$ $3.209$ $96$ 2.782.21 $753.60$ $2.820$ $97$ $3.01$ 2.21 $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ <td< td=""><td>84</td><td>1.70</td><td>2.22</td><td>880.50</td><td>5.577</td></td<>	84	1.70	2.22	880.50	5.577
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	85	1.60	2.16	1096.10	8.230
87 $2.13$ $2.26$ $701.20$ $2.560$ $93$ $2.16$ $2.12$ $1028.72$ $3.991$ $94$ $2.25$ $2.12$ $1024.20$ $3.482$ $95$ $2.56$ $2.22$ $832.30$ $3.209$ $96$ $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $1342.1$	86	2.20	2.20	854.30	4.080
93 $2.16$ $2.12$ $1028.72$ $3.991$ $94$ $2.25$ $2.12$ $1024.20$ $3.482$ $95$ $2.56$ $2.22$ $832.30$ $3.209$ $96$ $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $1883.75$ $4.333$ $105$ $2.73$ $2.19$ $1822.68$ $3.291$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $77$	87	2.13	2.26	701.20	2.560
94 $2.25$ $2.12$ $1024.20$ $3.482$ $95$ $2.56$ $2.22$ $832.30$ $3.209$ $96$ $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009$	93	2.16	2.12	1028.72	3.991
95 $2.56$ $2.22$ $832.30$ $3.209$ $96$ $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $134$	94	2.25	2.12	1024.20	3.482
96 $2.78$ $2.21$ $753.60$ $2.820$ $97$ $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $1342.18$ $7.293$ $165$ $3.03$ $2.13$ $1$	95	2.56	2.22	832.30	3.209
97 $3.01$ $2.21$ $846.20$ $2.010$ $98$ $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $1342.18$ $7.293$ $165$ $3.03$ $2.13$ $1202.15$ $5.620$ $166$ $3.46$ $2.09$	96	2.78	2.21	753.60	2.820
98 $3.32$ $2.22$ $1006.32$ $4.283$ $99$ $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $1342.18$ $7.293$ $165$ $3.03$ $2.13$ $1202.15$ $5.620$ $166$ $3.46$ $2.09$ $820.53$ $3.056$ $167$ $3.55$ $2.05$ <td< td=""><td>97</td><td>3.01</td><td>2.21</td><td>846.20</td><td>2.010</td></td<>	97	3.01	2.21	846.20	2.010
99 $3.52$ $2.21$ $928.21$ $3.983$ $100$ $3.20$ $2.20$ $887.02$ $3.858$ $101$ $3.52$ $2.22$ $1042.32$ $5.108$ $102$ $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $1342.18$ $7.293$ $165$ $3.03$ $2.13$ $1202.15$ $5.620$ $166$ $3.46$ $2.09$ $820.53$ $3.056$ $167$ $3.55$ $2.05$ $755.64$ $2.378$ $168$ $3.97$ $2.01$ <td< td=""><td>98</td><td>3.32</td><td>2.22</td><td>1006.32</td><td>4.283</td></td<>	98	3.32	2.22	1006.32	4.283
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	99	3.52	2.21	928.21	3.983
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	100	3.20	2.20	887.02	3.858
102 $3.21$ $2.21$ $923.29$ $4.293$ $103$ $3.48$ $2.20$ $843.03$ $3.291$ $104$ $3.01$ $2.19$ $883.75$ $4.333$ $105$ $2.73$ $2.19$ $817.12$ $4.679$ $106$ $3.33$ $2.20$ $938.39$ $3.892$ $107$ $2.95$ $2.19$ $1282.68$ $3.291$ $108$ $3.03$ $2.18$ $1092.17$ $3.829$ $109$ $3.11$ $2.19$ $1019.02$ $4.221$ $110$ $3.31$ $2.24$ $905.20$ $2.561$ $111$ $3.09$ $2.23$ $1233.54$ $3.629$ $112$ $2.87$ $2.19$ $1890.53$ $5.161$ $113$ $2.56$ $2.08$ $2166.1$ $7.350$ $114$ $2.66$ $2.16$ $845.67$ $3.356$ $115$ $2.68$ $2.22$ $777.20$ $2.435$ $116$ $2.98$ $2.15$ $902.30$ $4.930$ $117$ $2.52$ $2.06$ $1009.10$ $6.130$ $164$ $3.10$ $2.02$ $1342.18$ $7.293$ $165$ $3.03$ $2.13$ $1202.15$ $5.620$ $166$ $3.46$ $2.09$ $820.53$ $3.056$ $167$ $3.55$ $2.05$ $755.64$ $2.378$ $168$ $3.97$ $2.01$ $885.03$ $4.562$	101	3.52	2.22	1042.32	5.108
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	102	3.21	2.21	923.29	4.293
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	103	3.48	2.20	843.03	3.291
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	104	3.01	2.19	883.75	4.333
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	105	2.73	2.19	817.12	4.679
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	106	3.33	2.20	938.39	3.892
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	107	2.95	2.19	1282.68	3.291
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	108	3.03	2.18	1092.17	3.829
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	109	3.11	2.19	1019.02	4.221
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	110	3.31	2.24	905.20	2.561
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	111	3.09	2.23	1233.54	3.629
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	112	2.87	2.19	1890.53	5.161
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	113	2.56	2.08	2166.1	7.350
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	114	2.66	2.16	845.67	3.356
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	115	2.68	2.22	777.20	2.435
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	116	2.98	2.15	902.30	4.930
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	117	2.52	2.06	1009.10	6.130
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	164	3.10	2.02	1342.18	7.293
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	165	3.03	2.13	1202.15	5.620
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	166	3.46	2.09	820.53	3.056
168 3.97 2.01 885.03 4.562	167	3.55	2.05	755.64	2.378
	168	3.97	2.01	885.03	4.562

Table A.8: Characterization results from  ${\rm TiO}_2$  optimization process

# $\mathbf{A.5} \quad \mathbf{Y}_{2}\mathbf{O}_{3}$

	Deposition Source				Assist Source				trate		
No.	Press.	Ion	Ion	Ar	$O_2$	$\mathbf{RF}$	Ar	$N_2$	$\mathbf{RF}$	Temp	Angle
		Beam	Beam	Gas	Gas	Power	Gas	Gas	Power	1	0
	$10^{-4}$	Curr.	Volt.	Flow	Flow		Flow	Flow			
	[Torr]	[mA]	[V]	$[\mathrm{sccm}]$	[sccm]	[W]	$[\operatorname{sccm}]$	[sccm]	[W]	$[^{\circ}C]$	[°]
218	1.49	86	750	5	0	435	0	5	400	30	25
219	1.27	108	750	5	0	531	0	5	400	30	25
220	1.05	130	750	5	0	643	0	5	400	30	25
221	0.93	148	750	5	0	811	0	5	400	30	25
222	0.62	170	750	5	0	839	0	5	400	30	25
224	1.05	130	750	5	0	696	0	5	400	30	25
225	1.27	130	750	8	0	621	0	5	400	30	25
226	1.49	130	750	11	0	599	0	5	400	30	25
227	1.70	130	750	14	0	609	0	5	400	30	25
228	2.11	130	750	17	0	601	0	5	400	30	25
229	1.27	130	750	5	0	690	0	5	400	30	25
230	1.27	130	800	5	0	686	0	5	400	30	25
231	1.49	130	875	5	0	664	0	5	400	30	25
232	1.49	130	925	5	0	649	0	5	400	30	25
233	1.49	130	1000	5	0	633	0	5	400	30	25
234	1.70	130	750	5	0	674	0	10	400	30	25
235	2.73	130	750	5	0	694	0	15	400	30	25
236	3.14	130	750	5	0	701	0	20	400	30	25
237	1.05	130	750	5	0	675	0	0	400	30	25
240	0.84	108	750	5	0	736	0	5	400	110	25
241	0.84	108	750	5	0	673	0	5	400	190	25
242	0.84	108	750	5	0	674	0	5	400	270	25
243	0.84	108	750	5	0	758	0	5	400	350	25
253	1.27	130	750	5	0	710	0	5	400	30	25
254	1.27	130	750	5	0	705	0	5	300	30	25
255	1.27	130	750	5	0	703	0	5	200	30	25
256	1.27	130	750	5	0	701	0	5	500	30	25
257	1.27	130	750	5	0	681	0	5	600	30	25
284	3.34	108	750	5	0	718	0	5	400	30	25
285	3.34	108	750	5	0	715	0	5	400	30	30
286	3.34	108	750	5	0	703	0	5	400	30	35
287	3.34	108	750	5	0	708	0	5	400	30	15
288	3.34	108	750	5	0	709	0	5	400	30	20

Table A.9:	Table	of	optimization	conditions	for	$Y_2$	$_2C$	) <sub>3</sub>
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No	Deposition	Sheet	Refractive	Absorption	AFM
110.	Bate	Resistance	Index	Coefficient	Roughness
	[nm/sec]	$[10^9 \text{ O}]$	much	$[cm^{-1}]$	[nm]
010		102.1	1.60	105.94	
210	1.91	100.1	1.00	100.84	0.287
219	2.10	138.9	2.01	77.03 50.54	0.190 0.162
220	2.47	146.9	1.60	00.04 70.45	0.103
221	2.20	130.2 176.0	1.08	(3.43)	0.373
222	1.97	170.0 161.0	$1.09 \\ 1.72$	101.10	0.303 0.146
224 995	2.20	101.9 200.c	1.70	990.95	0.140 0.101
220	2.22	399.0 141.0	1.73	985.22	0.101
220	2.17	141.0	1.73	807.21	0.120
227	2.21	122.4	1.73	880.72	0.041
228	2.15	147.4	1.73	1069.10	0.049
229	2.32	130.2	1.73	142.78	0.318
230	2.49	137.0	1.73	129.90	0.184
231	2.64	128.9	1.73	122.37	0.217
232	2.69	150.7	1.73	125.04	0.284
233	2.80	220.2	1.73	133.36	0.335
234	2.30	441.5	1.71	135.56	0.232
235	2.21	87.3	1.72	148.60	0.168
236	2.14	155.2	1.73	138.07	0.126
237	2.36	12.27	1.75	1181.74	0.122
238	2.22	34.52	1.69	2503.81	0.384
239	1.56	0.48	1.75	1872.64	1.793
240	2.21	150.4	1.72	746.69	0.087
241	2.23	138.2	1.73	637.37	0.158
242	2.20	156.1	1.74	716.03	0.155
243	2.05	134.2	1.72	1047.03	0.157
244	2.20	140.5	1.75	1245.93	0.232
253	3.35	160.6	1.74	970.63	1.232
254	3.21	201.3	1.75	867.08	1.069
255	2.28	319.1	1.73	762.02	0.176
256	3.56	55.7	1.72	949.38	1.371
257	3.46	33.2	1.73	727.09	1.278
284	2.40	193.5	1.75	727.09	0.153
285	2.72	182.3	1.75	745.20	0.199
286	3.03	192.3	1.72	762.28	0.372
287	1.75	190.1	1.75	804.25	0.452
288	2.04	188.2	1.74	758.10	0.267

Table A.10: Characterization results from  $Y_2O_3$  optimization process

### A.6 ZnO

		Deposition Source				Assist Source				Substrate		
No.	Press.	Ion	Ion	Ar	$O_2$	$\operatorname{RF}$	Ar	$N_2$	$\mathbf{RF}$	Temp	Angle	
		Beam	Beam	Gas	Gas	Power	Gas	Gas	Power			
	$10^{-4}$	Curr.	Volt.	Flow	Flow		Flow	Flow				
	[Torr]	[mA]	[V]	[sccm]	[sccm]	[W]	[sccm]	[sccm]	[W]	$[^{\circ}C]$	[°]	
244	1.05	86	750	5	0	401	0	5	0	30	25	
245	1.27	108	750	5	0	430	0	5	0	30	25	
246	1.27	130	750	5	0	546	0	5	0	30	25	
247	1.91	148	750	5	0	799	0	5	0	30	25	
248	2.34	170	750	5	0	925	0	5	0	30	25	
249	1.27	130	800	5	0	875	0	5	0	30	25	
250	1.27	130	875	5	0	733	0	5	0	30	25	
251	1.27	130	925	5	0	644	0	5	0	30	25	
252	1.27	130	1000	5	0	604	0	5	0	30	25	
260	1.70	130	750	5	0	785	0	5	0	30	25	
261	1.91	130	750	8	0	679	0	5	0	30	25	
262	2.34	130	750	11	0	658	0	5	0	30	25	
263	2.52	130	750	14	0	611	0	5	0	30	25	
264	2.93	130	750	17	0	633	0	5	0	30	25	
265	1.70	130	750	5	0	735	0	5	0	110	25	
266	1.70	130	750	5	0	728	0	5	0	190	25	
267	1.70	130	750	5	0	746	0	5	0	270	25	
268	1.70	130	750	5	0	730	0	5	0	350	25	
271	1.49	130	750	5	0	821	0	5	400	30	25	
272	2.11	130	750	5	0	728	0	10	400	30	25	
273	3.14	130	750	5	0	726	0	15	400	30	25	
274	3.55	130	750	5	0	735	0	20	400	30	25	
275	0.84	130	750	5	0	779	0	0	400	30	25	
276	1.49	130	750	5	0	739	0	5	300	30	25	
277	1.49	130	750	5	0	754	0	5	200	30	25	
278	1.49	130	750	5	0	744	0	5	500	30	25	
279	1.49	130	750	5	0	731	0	5	600	30	25	
292	2.52	130	750	5	0	660	0	5	0	30	25	
293	2.52	130	750	5	0	659	0	5	0	30	30	
294	2.52	130	750	5	0	655	0	5	0	30	35	
295	2.52	130	750	5	0	650	0	5	0	30	15	
296	2.52	130	750	5	0	658	0	5	0	30	20	

Table A.11: Table of optimization conditions for ZnO

No.	Deposition	Sheet	Refractive	Absorption	AFM
	Rate	Index	Resistance	Coefficient	Roughness
	[nm/sec]	$[10^6 \Omega \text{ per square}]$	$[\mathrm{cm}^{-1}]$	[nm]	0
244	2.86	0.04	1.81	115.40	1.744
245	2.43	3.20	1.81	293.43	3.040
246	2.72	2.04	1.80	203.78	3.351
247	2.95	0.04	1.82	108.28	0.384
248	2.75	4.95	1.81	151.63	0.318
249	3.54	6.20	1.79	825.13	1.653
250	3.67	0.23	1.81	483.05	1.198
251	3.70	0.39	1.83	170.90	1.178
252	3.80	0.31	1.81	635.86	4.161
260	3.06	0.06	1.81	897.99	0.779
261	3.28	0.03	1.82	866.20	1.264
262	3.10	0.38	1.82	783.92	0.624
263	3.37	0.04	1.81	810.60	0.868
264	3.14	0.09	1.81	828.29	0.774
265	3.25	3.09	1.82	497.38	0.328
266	3.17	0.07	1.81	638.99	0.407
267	3.27	1.34	1.80	1193.95	0.714
268	3.30	1.46	1.79	1852.1	1.091
271	3.38	8.64	1.78	804.33	0.192
272	3.39	6.73	1.78	416.45	0.169
273	3.35	0.94	1.78	115.61	0.167
274	3.07	1.41	1.79	107.07	1.354
275	2.65	0.03	1.92	1488.14	2.921
276	1.89	1.04	1.79	1320.32	1.295
277	2.14	0.32	1.82	452.39	1.153
278	3.23	2.47	1.92	552.92	1.317
279	3.29	0.86	2.11	208.50	1.385
292	3.21	0.60	1.88	222.08	0.602
293	3.50	0.57	1.90	125.50	0.567
294	4.12	0.41	1.90	91.23	0.410
295	3.89	1.21	1.87	396.34	1.210
296	3.35	0.72	1.88	303.85	0.720

Table A.12: Characterization results from ZnO optimization process

### A.7 ZnSe

			Depc	sition S	Source		Ass	sist Sou	rce	Subs	trate
No.	Press.	Ion	Ion	Ar	$O_2$	$\mathbf{RF}$	Ar	$N_2$	$\mathbf{RF}$	Temp	Angle
		Beam	Beam	Gas	Gas	Power	Gas	Gas	Power	-	Ũ
	$10^{-4}$	Curr.	Volt.	Flow	Flow		Flow	Flow			
	[Torr]	[mA]	[V]	[sccm]	[sccm]	[W]	$[\operatorname{sccm}]$	[sccm]	[W]	$[^{\circ}C]$	[°]
324	0.62	86	750	5	0	641	0	0	0	30	25
325	0.62	86	800	5	0	633	0	0	0	30	25
326	0.82	86	875	5	0	604	0	0	0	30	25
327	1.05	86	925	5	0	619	0	0	0	30	25
328	1.05	86	1000	5	0	596	0	0	0	30	25
330	0.62	86	750	5	0	644	0	0	0	110	25
331	0.62	86	750	5	0	623	0	0	0	190	25
332	0.62	86	750	5	0	664	0	0	0	270	25
333	0.62	86	750	5	0	661	0	0	0	350	25
334	1.27	86	750	9	0	488	0	0	0	30	25
335	2.32	86	750	13	0	438	0	0	0	30	25
336	2.73	86	750	17	0	414	0	0	0	30	25
337	3.34	86	750	20	0	408	0	0	0	30	25
338	1.71	108	750	5	0	646	0	0	0	30	25
339	1.91	130	750	5	0	620	0	0	0	30	25
340	2.32	148	750	5	0	633	0	0	0	30	25
341	2.92	170	750	5	0	643	0	0	0	30	25
342	1.05	86	1000	5	0	459	0	0	0	30	20
343	1.05	86	1000	5	0	458	0	0	0	30	15
344	1.05	86	1000	5	0	456	0	0	0	30	30
345	1.05	86	1000	5	0	459	0	0	0	30	35
346	2.93	86	925	9	0	469	0	5	200	30	25
347	1.70	86	925	9	0	454	0	0	0	30	25
348	1.93	86	925	9	0	449	5	0	200	30	25
349	2.93	86	925	9	0	466	0	5	300	30	25
350	2.93	86	925	9	0	456	0	5	400	30	25
351	2.93	86	925	9	0	461	0	5	500	30	25
352	2.93	86	925	9	0	468	0	5	600	30	25
353	3.55	86	925	9	0	451	5	5	200	30	25
354	2.73	86	925	9	0	455	0	0	200	30	25
355	2.93	86	925	9	0	456	0	10	200	30	25
356	3.34	86	925	9	0	462	0	15	200	30	25
357	4.43	86	925	9	0	453	0	20	200	30	25

Table A.13: Table of optimization conditions for ZinSe
--

No.	Deposition	Refractive	Absorption	AFM
	Rate	Index	Coefficient	Roughness
	[nm/sec]		$[\mathrm{cm}^{-1}]$	[nm]
324	4.30	1.83	191.34	0.939
325	4.35	1.84	187.13	0.972
326	4.50	1.92	171.91	0.900
327	4.66	2.07	160.00	0.892
328	4.78	2.26	150.73	0.750
330	4.20	1.82	985.83	1.043
331	4.08	1.86	721.80	1.180
332	4.00	1.91	655.34	1.276
333	3.64	2.38	936.16	1.327
334	4.31	2.43	852.63	1.447
335	5.21	2.38	920.19	0.365
336	5.42	2.38	1290.88	0.889
337	5.50	2.40	1539.20	0.923
338	5.40	2.41	664.13	0.988
339	5.51	2.39	644.58	1.020
340	5.01	2.39	826.24	0.671
341	3.44	2.40	1667.56	1.900
342	4.14	2.42	1477.81	1.254
343	3.43	2.42	691.15	1.313
344	5.55	2.38	378.25	0.996
345	6.33	2.39	510.19	1.239
346	4.43	2.39	1592.79	0.920
347	4.27	2.45	615.39	0.991
348	4.60	2.39	829.29	1.256
349	4.27	2.42	598.02	1.029
350	4.60	2.41	441.96	1.123
351	4.57	2.38	199.81	1.304
352	4.58	2.37	451.76	1.350
353	5.29	2.42	705.31	2.392
354	4.97	2.44	729.29	1.838
355	4.73	2.39	592.10	1.570
356	4.01	2.38	629.21	1.599
357	3.97	2.37	720.99	1.599

Table A.14: Characterization results from ZnSe optimization process

### APPENDIX B

#### Figures of Optical Spectra

The purpose of this chapter is to provide experimentally measured transmittance and reflectance curves of all the substrates and materials discussed in this documentation. It should be noted that a slight variation in the infrared spectra of the semi-metal and dielectric materials can occur based on the thickness of the materials.



Figure B.1: FTIR measured transmittance and reflectance of a Si substrate



Figure B.2: FTIR measured transmittance and reflectance of a InP substrate



Figure B.3: FTIR measured transmittance and reflectance of a Gabs substrate



Figure B.4: FTIR measured transmittance and reflectance of PbTe



Figure B.5: FTIR measured transmittance and reflectance of  ${\rm SiO}_2$ 



Figure B.6: FTIR measured transmittance and reflectance of  $Si_3N_4$ 



Figure B.7: FTIR measured transmittance and reflectance of  ${\rm TiO_2}$ 



Figure B.8: FTIR measured transmittance and reflectance of  $Y_2O_3$ 



Figure B.9: FTIR measured transmittance and reflectance of ZnO



Figure B.10: FTIR measured transmittance and reflectance of ZnSe

### APPENDIX C

#### Comparisons of Techniques

This appendix provides characterization results from the comparisons of different materials deposited by EBE, IBSD, and PLD. For all samples, the thickness deposited was around 600 nm.

#### C.1 $Si_3N_4$



Figure C.1: AFM scans of  $Si_3N_4$  by PECVD and IBSD. Measured RMS values were 0.653 nm for PECVD  $Si_3N_4$  and 0.186 nm for IBSD.


Figure C.2: FTIR measured transmittance of  $Si_3N_4$  by PECVD and IBSD



Figure C.3: FTIR measured reflectance of  $Si_3N_4$  by PECVD and IBSD



Figure C.4: Absorption coefficient of  $Si_3N_4$  by PECVD and IBSD

# $C.2 TiO_2$



Figure C.5: AFM scans of TiO<sub>2</sub> by EBE and IBSD. RMS roughness values were 4.382 nm for EBE TiO<sub>2</sub> and 4.834 nm for IBSD TiO<sub>2</sub>



Figure C.6: FTIR measured transmittance of  $TiO_2$  by EBE and IBSD



Figure C.7: FTIR measured reflectance of  $\text{TiO}_2$  by EBE and IBSD



Figure C.8: Absorption coefficient of  $\mathrm{TiO}_2$  by EBE and IBSD

# $\mathbf{C.3} \quad \mathbf{Y}_2\mathbf{O}_3$



Figure C.9: AFM scans of  $\rm Y_2O_3$  by EBE and IBSD. RMS roughness values were measured to be 3.506 nm for EBE and 0.386 for IBSD



Figure C.10: FTIR measured transmittance of  $\mathrm{Y}_2\mathrm{O}_3$  by EBE and IBSD



Figure C.11: FTIR measured reflectance of  $\mathrm{Y}_2\mathrm{O}_3$  by EBE and IBSD



Figure C.12: Absorption coefficient of  $Y_2O_3$  by EBE and IBSD

# C.4 ZnO



Figure C.13: AFM scans of ZnO by PLD and IBSD. RMS roughness values were 2.670 nm for ZnO by PLD and 0.658 nm for ZnO by IBSD.



Figure C.14: FTIR measured transmittance of ZnO by PLD and IBSD



Figure C.15: FTIR measured reflectance of ZnO by PLD and IBSD



Figure C.16: Absorption coefficient of ZnO by PLD and IBSD



Figure C.17: PL measurement of ZnO by PLD and IBSD

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### Education

June 2008	PhD, Electric Northwestern	al Engineering University	Evanston, IL
	Dissertation	Dielectric Thin-Films Deposition for III-V I Imaging	by Ion-beam Sputtering Infrared Optoelectronic
	Advisor	Dr. Manijeh Razeghi	
	<ul> <li>Coursework completed in March 2005</li> <li>Passed oral qualifying exam in February 2007</li> <li>GPA 3.9/4.0</li> </ul>		
July 2004	MS, Electrica Georgia Instit	l Engineering tute of Technology	Atlanta, GA
	Thesis	Partitioning of Quant Based Circuits	tum-dot Cellular Automata
	Advisor	Dr. Sung Kyu Lim	
	• GPA 3.8/4.	0	
May 2003	BS, Compute University of	r Engineering Wisconsin	Madison, WI

• Area of specialization in VLSI Circuits and Architectures

- Graduated with High DistinctionGPA 3.7/4.0

Experience			
2004 - 2008	Graduate Research Assistant Center for Quantum Devices Evanston, IL		
	<ul> <li>Created high-quality dielectric and semi-metal structures for improved output power, temperature operation, thermal cycling lifetime, detectivity, quantum efficiency, zero-bias resistance-area, and luminous efficiency of infrared lasers, infrared detectors, and UV LEDs</li> <li>Reduced thermal management issues using selective area epitaxial growth techniques for lasers operating at high temperatures and high duty cycles</li> </ul>		
2003 - 2004	Graduate Research Assistant GT Computer-Aided Design Lab Atlanta, GA		
	<ul> <li>Achieved high throughput, low spatial area, and fast computation time with the design of physical automation tools for non-conventional architectures.</li> <li>Led teams of up to 5 students delegating workload, coordinating data, and assisting with problem solving techniques</li> <li>Succeeded in writing effective funding proposals for exploratory research grants</li> </ul>		
Summer 2003	Hardware Engineer Intern Hewlett-Packard Company Fort Collins, CO		
	<ul> <li>Designed hardware for the HP 507 digital camera, including collaboration with international vendors and various other types of engineers, achieving over 60% gross margin.</li> <li>Invented a mechanical technique for image stabilization</li> </ul>		
Summer 2002	Research Assistant Intern Berkeley Wireless Research Center Berkeley, CA		
	• Enhanced the throughput and runtime of error correction codes without sacrifice in bit error rate with a customized message-passing algorithm.		

- Implemented circuitry for enhanced performance of error correction codes with over an order magnitude reduction in computational complexity
- 2002 2003 Undergraduate Research Assistant Electromagnetics Lab Madison, WI
  - Developed a model for accurate simulation of the wave properties in a traveling wave tube amplifier with over 95%match with experimental measurements

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Honors and	Awards
2007 - 2008	Water P. Murphy Graduate Fellowship
2003, 2004	National Honor Society Graduate Research Fellowship
	Honorable Mention
2003 - 2004	Presidential Fellowship
2003 - 2004	Dean's Graduate Fellowship
2002 - 2003	Foliart Scholarship for Electrical Engineers
2002 - 2003	TDS Metrocom Engineering Scholarship
2002	Mortar Board Academic Achievement Award
2002	Dr. Brenda Pfaehler Award of Excellence
2002	Louise B. Truxdell Award
2001 - 2003	College of Engineering Leadership Scholarship
2001 - 2003	Ronald E. McNair Post-Baccalaureate Scholarship
1999 - 2003	Henry Vilas Scholarship
1000 2003	Powers Knapp Scholarship

- 1999 2003Powers-Knapp Scholarship
- 1999 2003 **TRIO** Award of Academic Excellence
- 1999 Kiernan Consulting Scholarship

#### **Technical Skills**

- Dielectrics and semi-metals
  - Techniques: Ion-beam sputtering deposition IBSD, Plasma-enhanced chemical vapor deposition PECVD, Electron-beam evaporation EBE
  - \_ Materials: Ge, GeO<sub>2</sub>, PbTe, SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, TiO<sub>2</sub>, TiN, Y<sub>2</sub>O<sub>3</sub>, ZnO, ZnSe, Ni, Ti, Pt, Au
- Semiconductors
  - Techniques: Molecular beam epitaxy MBE, Metal-organic chemical vapor deposition MOCVD
  - Materials: ING, GaAs, Gabs, GaN, Al<sub>2</sub>O<sub>3</sub>
- Material characterization techniques XRD, Hall, PL, AFM, SEM, ECV, Ellipsometry, FTIR, SIMS

- Semiconductor and microelectronic device fabrication, packaging,
  - Devices: Infrared lasers, Infrared detectors, UV light emitting diodes, field effect transistors
  - Tools: UV photolithography, Reactive ion etching, Chemical acid etching, Metallization, Electroplating, Rapid thermal annealing, Substrate thinning and polishing, Wire bonding, Die bonding, packaging
- Electronic design automation Integrated circuits, Printed circuit boards
- Design and simulation tools Mentor Graphics, Cadence, Synopsys, Xilinx
- Programming languages C++, Matlab\Simulink, Turbo Pascal, Java, Assembly, Basic, Fortran, VHDL, Verilog, HTML, SSHAFT
- Printed circuit board and integrated circuit board design, layout, and verification
- $\bullet$  Testing  $\$  fault analysis and modular integration

#### **Teaching Experience**

- Mentor, Graduate School Preparatory Training, Northwestern University
- Substitute Instructor and Teaching Assistant, Fundamentals of Solid-State Engineering, Northwestern University
- Teaching Assistant, Graduate Professional Communications in Engineering, Georgia Institute of Technology
- Mentor, College of Engineering Leadership Program, Wisconsin Wisconsin
- Course Tutor, Advanced Physics and Calculus Courses, University of Wisconsin
- Course Instructor, Introduction to Computer and Desktop Applications, UW Hospital and Clinics

#### **Professional Affiliations**

- Institute of Electronics Engineering (IEEE)
- International Society of Optical Engineering (SPIE)
- Society of Women Engineers (SWE)

#### Leadership Roles

- Manager of 1 (out of 3) research laboratory facilities at the Center for Quantum Devices
- Team leader of a group of 5 students at GT Computer-Aided Design Lab

- Team leader and manager of a group of 6 individuals for intra-network support at UW Hospitals
- President of Class of 2003 Powers-Knapp Scholar program at University of Wisconsin

#### Grants Awarded

- Automatic Placement Algorithms for Quantum Cellular Automata Nanoscale Exploratory Research (NER) Grant National Science Foundation (NSF)
- Placement and Routing for Polymorphic Computing Morphable Networked Micro-Architectures (MONARCH) Grant Defense Advanced Research Projects Agency (DARPA)

#### Presentations

- Techniques for High Quality SiO<sub>2</sub> Films Photonics West, San Jose, CA, January 2007
- Placement and Routing for Morphable Network Micro DARPA Review, Los Angeles, CA, February 2004
- Physical Design Automation Techniques for Quantum-dot Cellular based Automata NSF Review, Atlanta, GA, January 2004
- Computer Simulation of Capacitive Signal Sensors for Transmission Lines Undergraduate Research Symposium, Madison, WI, April 2003
- Capacitive Signal Sensors in a Helical Wave Transmission Line for Electomagnetic Applications
   11th Annual McNair National Research Conference, Delavan, WI, November 2002
- Design of a Low Density Parity Check Iterative Decoder SUPERB Research Symposium, Berkeley, CA, August 2002
- Digital Portable Voice Calibrator Undergraduate Research Symposium, Madison, WI, April 2002
- Digital Portable Voice Calibrator for Patients with Parkinson's Disease Engineering Projects in Community Services for Symposium, WI April 2002
- Digital Portable Voice Calibrator for Patients with Parkinson's Disease 2002 McNair National Undergraduate Research Conference, College Park, MD, February 2002

#### **Book Chapters**

- Semiconductor Device Technology Fundamentals of Solid State Engineering, 2nd Edition (edited and revised) Springer Publishing, February 2006
- Origins of CAD Tools for QCA Systems Nano, Quantum, and Molecular Computing: Implications to High Level Design and Validation Kluwer Academic Publishers, June 2004

#### Publications

- Y. Bai, S. R. Darvish, S. Slivken, W. Zhang, A. Evans, J. Nguyen, and M. Razeghi
   Room temperature continuous wave operation of quantum cascade lasers with watt-level optical power
   Appl. Phys. Lett. 92, 101105, (2008)
- S. Slivken, A. Evans, J. Nguyen, Y. Bai, P. Sung, S. R. Darvish, W. Zhang, and M. Razeghi Overview of quantum cascade laser research at the Center for Quantum Devices
   Proc. SPIE 6900, 6900B, (2008)
- M. Razeghi, M. B. Nguyen, P. Delaunay, D. M Hoffman, A. D. Hood, Y. Wei, and J. Nguyen Current state of Type-II InAs/GaSb Superlattices MWIR-LWIR Photodiodes and FPAs at the Center for Quantum Devices Proc. SPIE 6678, 27, (2007)
- Y. Bai, S. R. Darvish, S. Slivken, P. Sung, J. Nguyen, A. Evans W. Zhang, and M. Razeghi Electrically Pumped Photonic Crystal Distributed Feedback Quantum Cascade Lasers Appl. Phys. Lett. 91, 141123, (2007)
- A. Evans, S. R. Darvish, S. Slivken, J. Nguyen, Y. Bai, and M. Razeghi Buried Heterostructure Quantum Cascade Lasers with High Continuous wave Wall Plug Efficiency Appl. Phys. Lett. 91, 071101, (2007)
- M. Razeghi, A. Evans, Y. Bai, J. Nguyen, S. Slivken, S. R. Darvish and K. Mi *Current Status of High Performance Quantum Cascade Lasers at the*

Center for Quantum Devices Proc. of IPRM 6479, (2007)

- M. Razeghi, A. Evans, J. Nguyen, Y. Bai, S. Slivken, S. R. Darvish and K. Mi *High Power Mid- and Far-Infrared Lasers for Free Space Communication* Proc. of SPIE 6593, 65931v, (2007)
- M. Razeghi, A. Evans, J. Nguyen, S. Slivken, J. S. Yu, S. R. Darvish and K. Mi Mid-Infrared Quantum Cascade Lasers for High Temperature Applications Infrared Materials and Technology, (2007)
- J. Nguyen and M. Razeghi *Techniques for High-Quality SiO*<sub>2</sub> *Films* Proc. of SPIE 6479, 647953, (2007)
- S. Slivken, A. Evans, J. Nguyen, J. Yu, S. R. Darvish, K. Mi, and M. Razeghi High Power, Continuous-wave Quantum Cascade Lasers for MWIR and LWIR Applications Proc. of SPIE 6127, (2006)
- J. Nguyen, J. S. Yu, A. Evans, S. Slivken, and M. Razeghi Optical Coatings by Ion-beam Sputtering Deposition for Long Wave Infrared Quantum Cascade Lasers Appl. Phys. Lett. 89, 111113, (2006)
- W. W. Bewley, I. Vurgaftman, C. S. Kim, J. R. Meyer, **J. Nguyen** A. J. Evans, J. S. Yu, S. R. Darvish, S. Slivken, and M. Razeghi *High-Power Distributed Feedback Quantum Cascade Lasers* Proc. SPIE 6127, 612704, (2006)
- J. S. Yu, S. R. Darvish, A. Evans, J. Nguyen, S. Slivken, and M. Razeghi Room-Temperature Continuous-wave Operation of Quantum Cascade Lasers at λ ~ 4 μm Appl. Phys. Lett. 88, 041111, (2006)
- A. Evans, J. Nguyen, S. Slivken, J. S. Yu, S. R. Darvish, and M. Razeghi *Quantum Cascade Lasers Operating in Continuous-wave Mode Above 90°C at λ ~ 5.25 μm* Appl. Phys. Lett. 88, 051105, (2006)
- J. S. Yu, S. Slivken, A. Evans, S. R. Darvish, J. Nguyen, and M. Razeghi

High Power  $\lambda \sim 9.5 \ \mu m$  Quantum Cascade Lasers Operating Above Room Temperature in Continuous-wave Mode Appl. Phys. Lett. 88, 091113, (2006)

- Manijeh Razeghi, Allan Evans, Steven Slivken, Jae-Su Yu, Shaban Darvish, Burc Gokden, and Jean Nguyen Recent Advances in 3 - 5 Micron InGaAs/InAlAs/InP Quantum Cascade Lasers
   Proc. of CLEO 12, (2005)
- W. W. Bewley, I. Vurgaftman, C. S. Kim, J. R. Meyer, J. Nguyen, A. Evans, J. S. Yu, S. R. Darvish, S. Slivken, and M. Razeghi *Characterization and Analysis of Single-Mode High Power Continuous*wave Quantum Cascade Lasers J. Appl. Phys. 98, 084508, (2005)
- Manijeh Razeghi, Steven Slivken, Allan Evans, Jean Nguyen, Burc Gokden, Jae-Su Yu, and Shaban Darvish High Power, CW QCLs Operating at Room-Temperature Mid-Infrared Optoelectronics VII, (2005)
- M. Razeghi, J. S. Yu, A. J. Evans, S. Slivken, S. R. Darvish, J. E. David, J. Nguyen, B. Gokden, and S. Khosravani Quantum Cascade Lasers Progress and Outlook Proc. SPIE 5617, 221, (2004)
- Sung Kyu Lim, **Jean Nguyen**, Ramprasad Ravichandran, and Mike Niemer *Partitioning and Placement for Buildable QCA Circuits* ACM J. Emerging Tech. in Computing Systems 1, 50, (2004)
- Ramprasad Ravichandran, Nihal Ladiwala, Jean Nguyen, Mike Niemer, and Sung Kyu Lim Automatic Cell Placement for Quantum-dot Cellular Automata ACM Great Lakes Symposium on VLSI, 332, (2004)
- Jean Nguyen, Ramprasad Ravichandran, Sung Kyu Lim, and Mike Niemer Partitioning for Quantum-dot Cellular Automata based Circuits GIT-CERCS 20, (2003)
- Ramprasad Ravichandran, Nihal Ladiwala, **Jean Nguyen**, Sung Kyu Lim, and Mike Niemer Automatic Placement for Quantum Cellular Automata GIT-CERCS 31, (2003)

- J. Nguyen, M. C. Converse, and J. H. Booske Capacitive Signal Sensors in a Helical Wave Transmission Line for Electromagnetic Applications Proc. of McNair, 52, (2003)
- J. Nguyen, E. Yeo, and B. Nikolic Design of a Low-Density Parity-Check Iterative Decoder SUPERB Research Symposium (2002)
- J. Nguyen and B. Nikolic LDPC: An SISO Iterative Decoder Using Random Matrices UWJUR (2002)
- J. Nguyen, M. C. Converse, and J. H. Booske Computer Simulation of Capacitively-Coupled Signal Sensors for TWT Amplifiers Univ. of Wisconsin Undergrad. Research Symposium, (2002)
- M. Dombrowski, N. Young, E. Sparr, J. Nguyen, J. Jirka, E. Kho, and W. Tompkins Digital Portable Voice Calibrator for Patients with Parkinson's Disease Proc. of McNair, 113, (2002)
- J. Nguyen, M. C. Converse, and J. H. Booske Computer Simulation of Capacitive Signal Sensors for Transmission Lines UWJUR, (2002)
- J. Nguyen, M. C. Converse, and J. H. Booske Computer Simulation of Capacitively-Coupled Signal Sensors for Transmission Lines Univ. of Wisconsin Undergrad. Research Symposium, (2002)